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Polyaniline: A novel bridge to reduce the fire hazards of epoxy composites

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ABSTRACT

As a graphene-like two dimensional nanomaterial, MoS_2 had been considered as promising nanofillers for fabrication of polymer-based materials with high performances. However, its dispersion and functionalization represented a critical challenge. In present work, polyaniline (PANI) coating was successfully grown on the surface of exfoliated MoS_2 nanosheets by in situ polymerization method in order to improve the dispersion quality and interfacial interactions between MoS_2 and polymer matrix. The obtained PANI-MoS_2 hybrids were characterized through XRD, Raman spectrum, FTIR, TGA, XPS, TEM and further introduced into epoxy matrix. It was clearly observed that the addition of a PANI coating not only improved the dispersion of MoS_2 in the matrix and the interfacial bonding between MoS_2 and epoxy, but also obviously reduced the fire hazards of epoxy. By adding 2 wt% PANI-MoS_2, the peak heat release rate and total heat release values of epoxy composites were remarkably reduced by 49% and 22%, respectively, in comparison with those of neat epoxy. In addition, the amount of smoke produced and toxic CO released was inhibited obviously. The well dispersion, labyrinth barrier effect, catalytic charring effect of PANI-MoS_2 hybrids and combination effect between PANI and MoS_2 were believed to the primary source for the remarkable improvement of fire safety.

1. Introduction

Epoxy resins (EP) are one of the most important widely used thermosetting polymer materials and employed in many fields [1]. However, with a limiting oxygen index of only 19, the applications of EP in some areas are largely limited [2,3]. Moreover, a large amount of dense smoke combined with toxic effluent releases during combustion which seriously threatens the health and lives of human. Thus, developing novel and high efficiency flame retardants to improve the fire safety property of EP is imperative.

At present, there are multiple methods for improving the fire resistance of polymers. Polymer nanocomposites, with low loading of nanofillers, have attracted considerable interests for improving flame retardancy, smoke suppression and other properties simultaneously. Nanoplatelets with layered structure have been widely used to reduce the fire hazards of polymer materials in recent years, especially for montmorillonite, layered double hydroxides and graphene [4–6]. The obvious fire retarding effect of the 2D nanofillers are mainly attributed to so-called “tortuous path” effect of nanosheets, which can act as a barrier to inhibit the rapid heat and mass transfer and delay the release of pyrolysis gases of polymers during combustion [7].

As a member of 2D layered nanomaterials, MoS_2 has attracted much attention for reinforcing polymeric nanocomposites in the past few years due to its high surface area, good thermal insulating property and excellent mechanical properties [8]. MoS_2 or its derivatives have been used as multifunctional reinforcers in thermal, mechanical, and gas barrier properties of polymers at extremely low loading [9–14]. Additionally, due to its semiconductor characteristic, MoS_2 can be used as an excellent alternative to graphene in some special fields that require electrical insulation property and high dielectric constant of polymer composites [12]. Recently, benefited from the barrier effect and catalytic action, MoS_2 and its derivatives have been demonstrated as flame retardant nanoadditives to reduce fire hazards of various polymers [15–23]. However, the flame retardant efficiency of MoS_2 alone remains limited. Therefore, it is highly desirable to modify the surface characteristic of MoS_2 to improve its flame retardant performance in polymer matrices.

Similar to other 2D nanofillers, full utilization of MoS_2 in polymer nanocomposites will inevitably depend on their ability of achieving complete dispersion and sufficient compatibility in the polymer matrix [24]. However, aggregation and poor interfacial adhesion with polymers limit MoS_2 used as reinforcements in polymer composites. Thus, surface modification of MoS_2 nanosheets is generally essential to ensure a quality dispersion and sufficient interfacial interaction of MoS_2 nanosheets in a polymer matrix. The noncovalent functionalization of MoS_2 has been conducted using alkyl amine, chitosan and melamine

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phosphate, which are conducive to improve the compatibility and dispersibility of MoS_2 nanosheets in polymer matrices [20,24,25]. However, the lack of chemical bonding results in poor interfacial interaction between MoS_2 and polymer matrices, which in turn results in reduction of the effective reinforcement of MoS_2. The feasible route to harnessing the poor dispersibility and interfacial interactions would be to incorporate exfoliated MoS_2 nanosheets in polymer matrices via covalent interaction, which can provide active sites to form chemical bonds, acting as an ideal interface between MoS_2 and polymer matrices. Wang et al developed an in situ polymerization approach to covalently functionalize MoS_2 nanosheets and fabrication of polymer nanocomosites [26]. In our previous work, the exfoliated MoS_2 nanosheets were functionalized with 3-mercaptopropyl trimethoxysilane by ligand conjugation, and then incorporated into poly (vinyl alcohol) matrix by sol-gel technique [13]. However, most of the above-mentioned approaches have some serious limitations such as cost-effectiveness and scalability when applied in practical applications. In this regard, it is still highly desirable to exploit a novel strategy which is convenient and efficient but can improve the dispersibility of MoS_2 nanosheets and form strong interfacial interactions.

Polyaniline (PANI), consisting of alternative amine and imine groups in its backbone, is one of the most important conducting polymers and received special attention [27]. In the past few years, some studies have revealed the addition of PANI can improve the flame retardancy of polymer composites, which are mainly due to the char formation ability of conjugated PANI [28]. In addition, some studies have shown that PANI can serve as the coupling agent to improve the dispersion quality of nanofillers within epoxy matrix as well as enhance the interfacial adhesion by forming covalent bonding between PANI and EP molecules [29–31]. It is well known that the central transition metal Mo of MoS_2 benefits strong coordination with nitrogen atoms in conducting polymers such as polyaniline (PANI) or polypyrrole (PPy), which allows for the growth of conducting polymers onto the surface of MoS_2 [32,33]. Incorporating organic PANI with inorganic MoS_2 to form the hybrid material may preserve or even improve the major features of each phase, and new properties may result from the synergy of both components [34]. Although different kinds of PANI-MoS_2 hybrids have been reported, most of the efforts are focused on the electrical properties and catalysis performances [35–37]. Because of its conjugated structure and adjustable morphology, it is expected that PANI coating deposited on the exfoliated MoS_2 nanosheets can improve the dispersion and strengthen the interface adhesion between MoS_2 and EP matrix. However, there is no related report on the PANI assisted dispersion of exfoliated MoS_2 nanosheets within EP matrix as well as their thermal and fire safety properties.

Herein, the functionalized MoS_2 nanosheets with amine-rich surface are achieved by introducing a thin PANI nanocoating, looking forward to improving the dispersion and reinforcing the interaction between exfoliated MoS_2 nanosheet and EP matrix simultaneously. The aim of this work is to investigate the possibility of using PANI-MoS_2 hybrids for solving the dispersion problem of MoS_2 nanosheets and study the influences of amine-rich MoS_2 on the thermal and fire safety properties of EP composites.

2. Experimental

2.1. Materials

Molybdenum disulfide (MoS_2), *n*-hexane, acetone, concentrated hydrochloric acid, aniline, ammonium persulfate (APS) and 4,4-Diamino-diphenyl methane (DDM) all were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). *n*-Butyl lithium (1.6 M in hexane) and Epoxy (DGEBA, E-44) were purchased from Aladdin Industrial Corporation and Hefei Jiangfeng Chemical Industry Co. Ltd. (Anhui, China), respectively.

2.2. Preparation of PANI-MoS_2 hybrids

Chemically exfoliated MoS_2 was achieved through the sonication hydrolysis of lithium intercalated MoS_2 in deionized water, as reported in our previous report [11]. PANI-MoS_2 hybrids were synthesized by in situ chemical oxidative polymerization method. In a typical process, the exfoliated MoS_2 solution and aniline were added to a 1.0 M HCl solution with a weight ratio of 1:20 (MoS_2:aniline). The mixture was then ultrasonicated for 10 min and cooled in an ice bath below 5 °C. Then, a solution containing of APS (molar ratio of 1:2 to aniline) and HCl was added dropwise into the above mixture. The polymerization was carried out for 12 h in an ice-bath with the maintained mechanical stirring. Finally, the suspension was filtered and rinsed several times with deionized water and ethanol. The obtained products were dried at 60 °C for 24 h. Virgin PANI was prepared under the same procedure without the addition of exfoliated MoS_2 nanosheets.

2.3. Preparation of EP based composites

Typically, EP composites containing 2.0 wt% PANI-MoS_2 hybrids were fabricated as follows: 1.0 g PANI-MoS_2 hybrids were well dispersed into 100 mL acetone by ultrasonication. 49.0 g epoxy resins were preheated to 90 °C to reduce its viscosity and then poured into the above suspension under mechanical stirring and further sonicated for 1 h. The mixture was heated at 100 °C for 24 h to evaporate acetone. Thereafter, 9.8 g DDM was melted and dripped into the mixture under mechanical stirring. Afterwards the mixture was degassed under vacuum at 90 °C for 2 h to remove the entrapped air and residual solvents. Finally, the mixture was pre-cured at 100 °C for 2 h and post-cured at 150 °C for another 2 h. The same procedure was employed for fabrication of neat EP and EP composites with PANI and MoS_2.

2.4. Characterization

X-ray diffraction (XRD) was monitored using a Japan Rigaku D/Max-Ra rotating-anode X-ray diffractometer equipped with a Cu Kα tube and a Ni filter (λ = 0.1542 nm). Laser Raman spectroscopy (LRS) measurements were carried out at room temperature with a SPEX-1403 laser Raman spectrometer (SPEX Co., USA). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer (Nicolet Instrument Co., USA). X-ray photoelectron spectroscopy (XPS) was conducted using a VGESCALB MK-II electron spectrometer (Al Kα excitation source at 1486.6 eV). Thermogravimetric analysis (TGA) was carried out on a Q5000 thermoanalyzer instrument (TA Instruments Inc., New Castle, DE). Transmission electron microscopy (TEM) (JEM-2100F, Japan Electron Optics Laboratory Co., Ltd.) with an accelerating voltage of 200 kV was employed to investigate the morphology of samples and observe the dispersion state of MoS_2 nanosheets in EP matrix. Differential scanning calorimetry (DSC) was measured with a DSC Q2000 (TA Instruments Inc., USA). Flammability of the samples was characterized by cone calorimeter test (Fire Testing Technology, UK) according to ISO 5660. The fire toxicity was monitored by using a steady state tube furnace (SSTF) (ISO TS 19700), as reported in our previous literature [38,39]. Scanning electron microscopy (SEM) (JSM-6800F, JEOL) was employed to observe the fracture surface structure of EP composites and microstructures of the char residues.

3. Results and discussion

3.1. Characterization of PANI coated MoS_2 hybrids

XRD analysis and Raman spectrum are performed to validate the successful functionalization of MoS_2, as depicted in Fig. 1. Obviously, due to the easily restack of bare MoS_2 nanosheets, an intense diffraction peak appears at $2\theta = 14.4^\circ$ which is corresponded to the (0 0 2) plane of MoS_2 [14]. It indicates the reversion of bare MoS_2 nanosheets during