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The effective reinforcements of functionalized MoS_2 nanosheets in polymer hybrid composites by sol-gel technique

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ABSTRACT

In this work, siloxane group was grafted on the surface of exfoliated MoS_2 nanosheets by chemical conjugation with 3-mercaptopropyl trimethoxysilane and then the functionalized MoS_2 was incorporated into poly(vinyl alcohol) (PVA) matrix as reinforcements using sol-gel technique. The results of FTIR, TGA, XPS and TEM indicated that 3-mercaptopropyl trimethoxysilane was successfully grafted onto the surface of exfoliated MoS_2 nanosheets. The functionalized MoS_2 was well dispersed in PVA and no obvious aggregation of MoS_2 nanosheets was observed. The incorporation of functionalized MoS_2 nanosheets significantly enhanced the thermal properties, flame retardancy and mechanical properties of PVA films. The half weight loss degradation temperature of PVA films was increased from 298 to 416 °C and a 12 °C increment in the glass transition temperature was achieved with only 1.0 wt% functionalized MoS_2. Furthermore, the peak heat release rate and the tensile strength of PVA films was decreased by 52.5% and improved by 98.4%, respectively, compared to that of neat PVA. These excellent reinforcements were mainly attributed to well dispersion of MoS_2 nanosheets in the polymer matrix and strong interfacial adhesion between the two components. This work demonstrated herein will provide a promising route to fabricate MoS_2-based polymer nanocomposites with excellent performances.

1. Introduction

Poly(vinyl alcohol) (PVA), as one kind of water soluble and biocompatible polymer, has attracted intensive attention in various applications such as coating, textile sizing, and packaging films [1]. Nevertheless, insufficient mechanical, thermal stability and flammability properties of pure PVA have limited its wider applications in some fields. In the past few decades, polymer nanocomposites consist of polymer matrix and nanofillers have aroused tremendous interests due to the excellent performances of the obtained polymer materials, especially for the layered nanofillers. When the layered nanofillers are well dispersed in the polymer matrix, the incorporation of nanofillers with low loadings can trigger substantial improvements in mechanical properties, thermal stability, fire resistance, and gas permeability [2]. As well known, the typical layered nanofillers including MMT, LDH and graphene have been proven to impart effective reinforcement and flame retardancy with PVA matrix owing to their lamellar structure and high aspect ratio. Mallakpour et al. had prepared a coexistence of exfoliated and intercalated Cloisite Na^+/Val layers structure in the PVA matrix which improved the thermal stability property of the resulting films obviously [3]. Liu and his co-author had reported that the LDH nanoplates were uniformly dispersed in PVA matrix and the mechanical and thermal properties of the composites were improved obviously [4]. Bao et al. studied the influences of graphite oxide and graphene on the structure and properties of PVA nanocomposites contrastively and discussed the mechanism for the property enhancements [5].

As an emerging layered 2D nanomaterial, it has been reported recently that a monolayer of MoS_2 has high surface areas, superb thermal stability and excellent mechanical properties, and show great potential as reinforcements for polymer materials [6]. Therefore, it is expected that the MoS_2 can become a new generation of reinforcements to fabricate high performance polymer materials. In the past few years, some reports have demonstrated that incorporation of exfoliated MoS_2 nanosheets at extremely low loading can endow polymer matrices with prominent thermal and mechanical properties [7–10]. In addition, MoS_2 or its derivatives have been reported as flame retardant nanoadditives to improve the flame retardancy of various polymers such as PVA, PS, PMMA, EP and TPEE [9,11–17]. However, as with graphene, complete

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utilization of MoS_2 sheets in polymer nanocomposite inevitably depends on their dispersibility and sufficient compatibility in the polymer matrix. But actually, the exfoliated MoS_2 nanosheets have a tendency to agglomerate and even restack in polymer matrices owing to their large specific surface area and van der Waals interactions, which results in the reduced efficiency for reinforcement [18]. In addition, the formation of a strong bonding between polymer matrix and nanofillers is another key factor to improve the properties of composites obviously. Consequently, the exfoliated MoS_2 nanosheets are necessary to be functionalized before incorporation into polymer matrices.

An effective way to overcome the agglomeration and enhance the compatibility and interfacial interactions between MoS_2 nanosheets and polymer matrix is the chemical modification of exfoliated MoS_2 nanosheets via noncovalent and covalent interaction. In our previous work, surfactant molecules, chitosan and melamine phosphate have been used to modify the exfoliated MoS_2 nanosheets through noncovalent interaction, these modification methods are conducive to improve the compatibility and dispersibility of MoS_2 nanosheets in polymer matrices [7,16]. However, there is no substantial improvement for the interfacial interactions between MoS_2 nanosheets and polymer matrix. 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. The covalent functionalization of MoS_2 nanosheets not only significantly improves the dispersion of MoS_2 nanosheets, but also forms strong interfacial interactions with host polymer via covalent linkages [19].

Surface modification of exfoliated MoS_2 nanosheets by covalent functionalization can provide active sites to form chemical bonds, acting as an ideal interface between the MoS_2 and appropriate polymer matrices. However, different from graphene oxide, there are no functional groups on surface of MoS_2 nanosheets, which makes it difficult to be decorated directly. Fortunately, some literatures have demonstrated that many defects of S atoms on MoS_2 will be generated after being chemically exfoliated, which shows that it is possible to modify the internal and perimeter edges of MoS_2 using thiol ligand functionalization [20]. Zhou et al. have reported that carboxyl functional group decorated MoS_2 nanosheets can be obtained by chemical conjugation of mercaptopropionic acid with chemically exfoliated MoS_2 nanosheets [21]. Wang et al. chemically exfoliated bulk MoS_2 into nanoplatelets, and functionalized using lipoic acid via disulfide conjugation. The lipoic acid functionalized MoS_2 nanosheets offered carboxyl terminals as the initiator for in situ ring-opening polymerization of 3-caprolactam to fabricate nylon-6 nanocomposites. The covalent functionalized MoS_2 nanosheets dispersed well in nylon-6 matrix and induced significant thermal stabilization and mechanical reinforcement [22].

As far as we know, various kinds of siloxanes have been widely used as coupling agents between glass substrates and polymeric resins. The coupling process can be accomplished via the chemical reaction between the trialkoxy groups of silane molecules and the hydroxyl groups on the glass substrates. Recently, different types of silanes have been developed to act as multifunctional and crosslinking agents between graphene sheets and the polymeric substrate to produce functionalized graphene aerogels [23,24]. In addition, many literatures have reported that silane precursors are used to modify PVA by sol-gel reaction to form PVA/silica hybrid composites at a molecular level [25,26]. These hybrid composites usually exhibit good thermal stability, mechanical, separation properties and do little harms to the physical performance of polymers. Sol-gel chemistry has become one of the most exciting fields in the synthesis of novel functional nanomaterials and provides the possibility to form covalent bonds between the organic phases and inorganic phases [27]. However, to the best of our knowledge, there are no literatures reported on the application of exfoliated MoS_2 nanosheets as reinforcements in polymer composites by sol-gel method up to date.

Herein, the PVA/functionalized MoS_2 hybrid films are fabricated by the sol-gel method in aqueous solution, as shown in Fig. 1. Functionalization of MoS_2 nanosheets with 3-mercaptopropyl trimethoxysilane (MTS) was completed by the ligand conjugation between the chemically exfoliated MoS_2 nanosheets and the thiol groups of MTS. The MTS was selected as the "bridge" to covalently connect MoS_2 nanosheets with PVA matrix. The covalent functionalization will improve the compatibility and interfacial interactions between PVA matrix and exfoliated MoS_2 nanosheets, which leads to effective reinforcements in thermal, flame retardance and mechanical properties of the PVA films.

2. Experimental

2.1. Materials

PVA (polymerization degree 1750 ± 50, CP), molybdenum disulfide (MoS_2, AP), tetrahydrofuran (THF, AP) and n-hexane (AP) were purchased from the Sinopharm Chemical Reagent Co., Ltd. The n-butyl lithium (2.2 M in hexane) was purchased from Alfa Aesar without further purified. 3-mercaptopropyl trimethoxysilane (MTS) was purchased from J&K Chemical Ltd. All the other starting materials used in this work were of analytical grade and used without further purification.

2.2. Fabrication of MTS-functionalized MoS_2 nanosheets

The fabrication route of the MTS-functionalized MoS_2 nanosheets was shown in Fig. 1a and b. The chemically exfoliated MoS_2 nanosheets were prepared by lithium intercalated and ultrasonication hydrolysis method according to our previous work [9]. Then the colloidal suspension of chemically exfoliated MoS_2 nanosheets was mixed with excess amount of MTS which were dissolved in THF under stirring for 8 h. The functionalized MoS_2 (MoS_2-MTS) was collected by centrifugation, several washing steps with THF and water. Most of the functionalized MoS_2 were redispersed in water to form the suspension, and a small portion was dried at 60 °C for 24 h in vacuum oven for characterization.

2.3. Preparation of PVA/functionalized MoS_2 hybrid films

To prepare PVA/functionalized MoS_2 hybrid films, PVA was first dissolved in deionized water with a concentration of 10 mg mL^{-1} at 95 °C in a three neck flask. The required MoS_2-MTS aqueous suspension was dripped into the abovementioned PVA solution. Then, HCl solution was added to catalyze crosslink with stirring at 60 °C for 10 h. At last, the aqueous mixture was sonicated for 20 min and poured into telfon petridishes and heated to 40 °C in oven for approximately 24 h to form flat membranes. The obtained membranes were further heated at 60 °C for 24 h to remove residual water and cut into pieces for tests. The content of the MoS_2-MTS in the PVA hybrid films was defined as 0.5 wt% and 1.0 wt%. In addition, a similar procedure was used to prepare pure PVA films.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 6700 spectrometer (Nicolet Instrument Corporation, Madison, WI). X-ray photoelectron spectroscopy (XPS) spectra were performed on VG ESCALB MK-II electron spectrometer. Transmission electron microscopy (TEM) images were obtained on a Hitachi model H-800 transmission electron microscope with an accelerat-