



Fabrication and characterization of graphene oxide-reinforced poly(vinyl alcohol)-based hybrid composites by the sol-gel method



Shu-Dong Jiang, Zhi-Man Bai, Gang Tang, Yuan Hu*, Lei Song

State Key Laboratory of Fire Science, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China

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ABSTRACT

Functionalized graphene oxide-reinforced poly(vinyl alcohol) hybrid composites were prepared by using the sol-gel method. This method not only provided a “green” strategy for fabricating the graphene oxide-based composites, but also realized the covalent functionalization of graphene oxide nanosheets with polymer matrix. The morphology, thermal, fire resistance and mechanical properties of the f-GNS/poly(vinyl alcohol) hybrid composites were systematically studied. The transmission electron microscopy analyses demonstrated that f-GNS was homogeneously dispersed in the poly(vinyl alcohol) matrix. Combining with a series of analyses and characterizations, it was observed that the functionalization of graphene oxide with conjugated organosilanes was favorable for improving mechanical, thermal properties and flame retardance of the composites, which was mainly attributed to the homogeneous dispersion of functionalized graphene oxide in the polymer matrix and strong interfacial interactions between the two components.

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1. Introduction

Organic–inorganic hybrid materials lie at the interface of the organic and inorganic realms. These materials are formed by the combination of nanoscale inorganic and organic domains, and offer exceptional opportunities not only to combine the important properties from both materials but also to create entirely new compositions with truly unique properties [1–3]. In the early ages of the polymer composites research, silicates, double hydroxides (LDHs) and carbon nanotubes (CNTs) were the most widely investigated [4–6]. However, in the present, graphene-based materials already dominated in this field [7,8]. These hybrid composites are new generation functional materials applied in many fields, such as biology, environment, electronics, energy, mechanics, medicine, membrane separation and optics [9,10].

Poly(vinyl alcohol) (PVA) is one of the most important materials with many desirable characteristics, such as biocompatibility, biodegradability, and water-solubility. Nevertheless, pure PVA suffers from weak physical–chemical stability and thermal resistance, and does not offer sufficient excellent properties for certain applications [11,12]. According to the reported literatures, many efforts were made to prepare high-performance PVA composites. Bao et al. studied contrastively the structure and properties of graphene/PVA

composites and graphite oxide/PVA composites and discussed the mechanism for the property enhancements [13]. In addition, researchers successfully used silane precursors to modify PVA to form polymer/silica organic–inorganic hybrid composites at a molecular level through sol-gel reaction [14,15]. These hybrid composites based on Si–O–C and Si–O–Si networks in the polymer matrix usually have higher thermal and mechanical stabilities than traditional polymer composites [16,17]. Specifically, silica hybridization can easily adjust the polymer microstructure and introduce new functional groups into the polymer matrix for enhancing the functional performance of polymer composites [18–20]. The crosslinked polymers composites with network structures of physically or chemically cross-linked has attracted much attention, which can alter the thermal, mechanical properties and flame retardancy of the materials [21–23]. However, to our best knowledge, little work has been reported the preparation of PVA hybrid composites through covalently connecting graphene oxide nanosheets with PVA matrix, using siloxane as the cross-linking agent.

Herein, the functionalized graphene oxide sheets/PVA (f-GNS/PVA) hybrid composites were fabricated by the sol-gel method in aqueous solution, as illustrated schematically in Fig. 1. Functionalization of graphite oxide (GO) with 3-aminopropyltriethoxysilane (APTES) was realized through the nucleophilic substitution reaction between the epoxide groups of graphite oxide and the amine groups of APTES. The silane coupling agent, APTES, was

* Corresponding author. Tel./fax: +86 551 3601664.

E-mail address: yuanhu@ustc.edu.cn (Y. Hu).

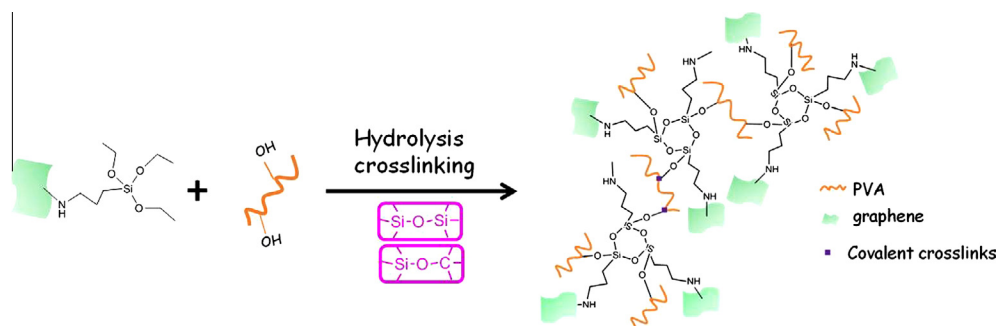


Fig. 1. Illustration for preparation route of PVA hybrid composites.

selected as the “bridge” to covalently connect graphene oxide sheets (GNS) with PVA matrix. The covalent functionalization of GNS would afford better compatibility and interfacial interactions with the PVA matrix, thereby was expected to endow the PVA matrix with the enhanced thermal, flame retardance and mechanical properties.

2. Experimental

2.1. Materials

PVA (polymerization degree 1750 ± 50 and saponification degree 98%, CP), Graphite powder, concentrated sulfuric acid (98%), sodium nitrate, potassium permanganate, 30% H_2O_2 solution, hydrochloric acid, and hydrazine hydrate (80%) were of reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). N,N'-dicyclohexylcarbodiimide (DCC, 99%) and 3-aminopropyltriethoxysilane (APTES, 99%) were of analytical grade and obtained from Aldrich (America). All the reagents were used without further purification.

2.2. Fabrication of APTES-functionalized GNS

GO powders were synthesized from graphite by Hummers method [24]. Graphite oxide (50 mg) and DCC (25 mg, as cat.) were dispersed in APTES (50 ml) followed by ultrasonication for 1 h, and the black and homogeneous mixtures were stirred and heated to 70 °C for 24 h. Afterwards, the resulting APTES-functionalized GNS were centrifuged, washed with absolute ethanol and then dried under vacuum.

2.3. Preparation of f-GNS/PVA hybrid composites

To prepare f-GNS/PVA hybrid composites, PVA was dissolved in deionized water at 95 °C to form PVA aqueous solution. The required f-GNS aqueous suspension was dripped into the PVA solution. Then, HCl solution (1 mol L^{-1}) was added to catalyze crosslink with stirring at 60 °C for 10 h. At last, the blending was cast onto Teflon-plates and dried at 40 °C in an oven for 24 h to form flat films which were peeled off and further heated at 80 °C for 48 h to remove residual water. The obtained films were cut into pieces for tests. The formulations of f-GNS/PVA hybrids are listed in Table 1.

2.4. Characterization

Several analytical techniques were used to characterize the synthesized products. The powder X-ray diffraction (XRD) patterns of the as-synthesized samples were recorded with a Japan MapAHF X-ray diffractometer equipped with graphite-monochromatized

Table 1

Formulation of f-GNS/PVA hybrid composites.

Sample	Component
PVA	Pure PVA
PVA1	0.5 wt% f-GNS/PVA
PVA2	1 wt% f-GNS/PVA
PVA3	2 wt% f-GNS/PVA

Cu $K\alpha$ irradiation ($\lambda = 0.154056 \text{ nm}$), employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range of 3–60°. Fourier transform infrared (FTIR) spectra were recorded using samples pelletized in KBr powder and a Nicolet spectrophotometer (ZOSX). Microstructures of the char residues were observed by JEOL JSM-2010 field-emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) images were obtained on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV. Before observation, GO and f-GNS were dispersed in deionized water followed by ultrasonication for 30 min. The homogeneous mixtures were dripped on carbon-coated copper grids. PVA nanocomposites were cut into ultrathin sections using a CM1900 microtome (Leica, Wetzlar, Germany). The ultrathin sections were transferred from liquid nitrogen to carbon-coated copper grids and then observed by TEM. X-ray photoelectron spectra (XPS) were taken on a Thermo ESCALAB 250 X-ray photoelectron spectrometer with Al $K\alpha$ radiation. Elemental analysis was performed on a Vario EL III elemental analyzer. Solid-state ^{29}Si NMR spectra were recorded using a Bruker AV400 NMR spectrometer (400 MHz). Thermogravimetric analyses (TGA) of samples were carried out with a Q5000 thermal analyzer (TA Co., USA) from 50 °C to 700 °C at a heating rate of $20^\circ \text{ C min}^{-1}$ in air atmosphere. The fire resistance of samples was evaluated with a microscale combustion calorimeter (Govmark Organization, Inc., Farmingdale, NY) according to ASTM D7309-07. The tensile strength and elongation at break was measured with an electronic universal testing instrument according to GB13022-91 (MTS System Co., Ltd., China) with an initial length of 20 mm at a crosshead speed of 50 mm min^{-1} . Nanocomposite films were cut into special pieces, and six parallel runs were performed for each sample to obtain averages. Dynamic mechanical analysis (DMA) was performed using a DMAQ800 apparatus (TA Instruments Inc.) at a fixed frequency of 10 Hz in the temperature range from 30 to 100 °C.

3. Result and discussion

3.1. Structural properties

XPS analyses were used to elucidate the surface composition of GO and f-GNS, which could provide information of the interactions between GO and APTES. The higher resolution XPS spectra in the C_{1s} region of (A) GO and (B) f-GNS are presented in Fig. 2. Fig. 2A

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