



Magnetic and mechanical properties of polyvinyl alcohol (PVA) nanocomposites with hybrid nanofillers – Graphene oxide tethered with magnetic Fe₃O₄ nanoparticles

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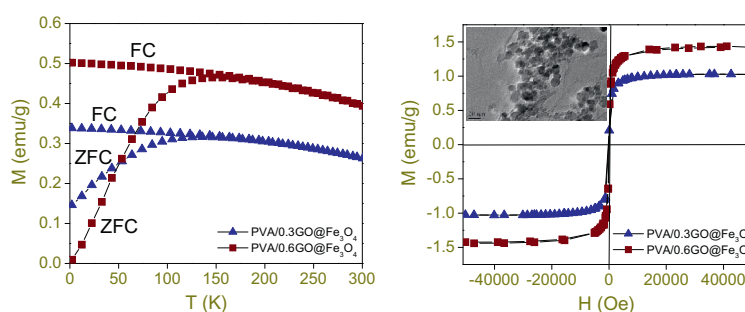
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HIGHLIGHTS

- PVA nanocomposites with GO@Fe₃O₄ NP hybrid fillers were prepared.
- These nanocomposites exhibit superparamagnetic behavior.
- 0.3 wt% of GO nanofillers resulted in 230% increase in tensile failure strain.
- Fe₃O₄ nanoparticles and GO nanosheets significantly improved thermal stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic nanoparticle-attached graphene oxide nanosheets (GO@Fe₃O₄) were first synthesized and then employed as nanofillers to create a polyvinyl alcohol (PVA) nano-composite with magnetic characteristics. When subjected to an applied magnetic field, this new nanocomposite exhibited superparamagnetic behavior, with the saturation magnetization strength depending on the content of GO@Fe₃O₄ hybrid nanofillers. Tensile tests were conducted to characterize the mechanical properties of the PVA nanocomposites with GO nanosheets, Fe₃O₄ nanoparticles and hybrid GO@Fe₃O₄ nanofillers. The addition of 0.3 wt% of GO nanosheets resulted in substantial increase (230%) in failure strain from 72% for the neat PVA film to 237% for the PVA/0.3GO nanocomposite films. This dramatic improvement in ductility was shown, through detailed examination of the fracture surface of the tensile specimens, to originate from the highly aligned, layered GO nanoplatelets during the tensile fracture process. Furthermore, the introduction of Fe₃O₄ nanoparticles and GO nanosheets has also significantly improved the thermal stability of PVA.

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1. Introduction

Polymer nanocomposites are a new class of promising materials for fabricating future multifunctional and lightweight structures. The unique properties of graphene have attracted intense research interests in developing new composites with graphene-based materials [1,2]. Graphene oxide (GO), synthesised from inexpensive graphite powders [3,4], is currently a major precursor for cost-effective and bulk production of graphene-based

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materials. GO can be prepared by oxidizing graphite with strong oxidants followed by gentle exfoliation. With further treatment using chemical, thermal, photocatalyst, photo radiation and electrochemical methods [5,6], exfoliated graphite can be reduced to form chemically modified graphene (i.e. r-GO) that are suitable as nanofillers in nanocomposites.

To obtain good mechanical, thermal and electrical properties, it is essential to achieve uniform dispersion of nanofillers in the polymer matrix [7,8]. Since GO can be easily exfoliated and dispersed in water, its excellent solvent processability is particularly favorable for preparing composite materials by premixing it with matrix. As a water-soluble polymer, polyvinyl alcohol (PVA) has been broadly used as the matrix material to investigate the effect of graphene-based nanofillers on nanocomposite properties [9,10].

Carbon nanotubes and magnetic nanoparticles have been investigated for a wide range of applications in sensors, magnetic energy storage, environmental remediation, heterogeneous catalysts and drug delivery. Due to the large surface area and unique mechanical and electrical properties of graphene/GO nanosheets, the hybrids of magnetic nanoparticles and graphene/GO would have better functionalities and performance in the above application areas [11,12]. Cong et al. have recently successfully synthesized reduced GO sheets decorated with monodisperse magnetite nanoparticles. Their approach creates a new class of graphene-based composites with unique properties for potential applications such as MR imaging or protein separation [13]. The magnetic response from the hybrid magnetic nanosheets can also facilitate with the alignment of nanofillers in a polymer matrix under magnetic field, aiming at fabricating composites with directional properties and functions [14].

In the present investigation, GO nanosheets tethered with magnetic Fe_3O_4 (magnetite) nanoparticles (NPs), were firstly synthesized and characterized. These magnetic nanofillers were then employed in a PVA matrix to create multifunctional nanocomposites. Magnetic, mechanical properties and microstructural morphology of these nanocomposites were characterized. The results were compared with those pertinent to composite films with GO nanofillers only.

2. Materials and methods

2.1. Synthesis of graphene oxide nanosheets

GO nanosheets were prepared using a modified Hummers method [15]. Graphite flake (10 g) and sodium nitrate (7.5 g) were added to 300 mL of sulfuric acid (98%), and then 40 g of potassium permanganate was added to the reaction slowly in one hour. The mixture was stirred at room temperature for 3 days, followed by adding 1 L of hydrogen peroxide solution (1% in water). Subsequently, the mixture was filtered and washed with deionized water until pH 7. The resulting black cake was re-dispersed in deionized water to give a dark brown dispersion, which was then subjected to dialysis for one week to remove the residual salts and acids. The brown suspension was dried at 40 °C under vacuum. GO suspension was then obtained by sonicating the as-prepared black solid in water under ambient condition for 30 min.

2.2. Synthesis of Fe_3O_4 magnetic NPs

Fe_3O_4 NPs were prepared by co-precipitating Fe^{2+} and Fe^{3+} ions in aqueous ammonia solution [16]. 1.5 M NH_4OH solution was dropped into 200 mL of deionized water containing 0.85 g of ferric (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Aldrich) and 0.30 g of ferrous (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Merck) (molar ratio 2:1) under a N_2 atmosphere, while the solution was stirred rapidly.

The solution was controlled at pH 8 by slowly adding NH_4OH . The resulting precipitate was then stirred for 2 h. After triple washes with deionized water and ethanol, the Fe_3O_4 precipitate was re-suspended in 100 mL deionized water.

2.3. Preparation of $\text{GO@Fe}_3\text{O}_4$ hybrid nanosheets and nanocomposite films

The prepared GO and Fe_3O_4 water solutions were sonicated for 10 min respectively before mixing in a rotary suspension mixer overnight with a GO: Fe_3O_4 weight ratio of 1:4. PVA (weight-average molecular weight = 146,000–186,000, 98–99% hydrolyzed, Aldrich) was used as received and dissolved in water under constant stirring at 110 °C to form a 5 wt% PVA water solution. GO nanosheets and Fe_3O_4 NPs were dispersed in water by sonication for 10 min and then mixed with the prepared PVA solution at different weight ratios, respectively. The $\text{GO@Fe}_3\text{O}_4$ composite fillers were also dispersed in water by sonication for 5 min before mixing with the PVA solution. Six different types of PVA nanocomposite films were prepared with (i) 0.3 wt% of GO, (ii) 0.6 wt% of GO, (iii) $\text{GO@Fe}_3\text{O}_4$ fillers containing 0.3 wt% GO (denoted as PVA/0.3GO@ Fe_3O_4), (iv) $\text{GO@Fe}_3\text{O}_4$ fillers containing 0.6 wt% GO (denoted as PVA/0.6GO@ Fe_3O_4), (v) 1.2 wt% of Fe_3O_4 NPs, and (vi) 2.4 wt% of Fe_3O_4 NPs. The films were dried at ambient temperature in a fume hood and then in a 60 °C oven for 8 h.

2.4. Characterizations

Tensile tests were performed on an Instron 30 K tester with gauge length of 10 mm and loading rate of 2 mm/min. Five specimens were tested for each material type. The sample morphologies and structures were investigated by atomic force microscopy (AFM) on a Bruker MultiMode-8 tester, transmission electron microscopy (TEM) on a JEOL-2100 with an acceleration voltage of 200 kV, scanning electron microscopy (SEM) on a Zeiss Supra 55VP. X-ray photoelectron spectroscopy (XPS) data were collected on a VG ESCALAB 220-iXL spectrometer with a monochromatic Al $K\alpha$ source (1486.6 eV) at 150 W (15 kV, 10 mA). X-ray diffraction (XRD) data were obtained on a PANalytical's X'Pert Power X-ray Diffraction (40 kV, 30 mA) with Cu $K\alpha$ radiation at a scanning rate of 2.4° min^{-1} . Magnetic properties ($M-H$ curves) were measured at room temperature (300 K) with a Quantum Design MPMS-5 DC-SQUID (superconducting quantum interference device) susceptometer. Field cooling (FC) and zero field cooling (ZFC) curves were recorded.

3. Results and discussion

3.1. Morphology and magnetic property of $\text{GO@Fe}_3\text{O}_4$ hybrid nanosheets

Fig. 1 presents the AFM image and the XPS spectrum of the GO nanosheets prepared. The XPS spectrum of GO indicates three main components that corresponds to the carbon atoms in different functional groups: the nonoxygenated C–C bond, the C–O bond (epoxy and hydroxyl) and the carboxylate C=O from carboxylic acid [17]. The morphology of $\text{GO@Fe}_3\text{O}_4$ hybrid nanosheets is shown in Fig. 2. Fig. 2a–c shows the AFM images and section analysis of $\text{GO@Fe}_3\text{O}_4$. The hybrid nanosheets exhibit a folded structure with their surfaces densely covered with Fe_3O_4 NPs, which have lateral dimension of a few microns and thickness of around 50 nm (since both sides of the GO nanosheets were tethered with Fe_3O_4 NPs). The TEM image in Fig. 2d also shows the densely deposited Fe_3O_4 NPs with an average size of 11.6 nm (from 50 measurements). The prepared hybrid nanosheets were shown to be magnetic, since the $\text{GO@Fe}_3\text{O}_4$ hybrid fillers in water (Fig. 2e)

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