

Preparation and Characterization of Graphene/Poly(vinyl alcohol) Nanocomposites

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ABSTRACT: Graphene (GE)-based nanocomposites are emerging as a new class of materials that hold promise for many applications. In this article, we present a general approach for the preparation of GE/poly(vinyl alcohol) (PVA) nanocomposites. The basic strategy involved the preparation of graphite oxide from graphite, complete exfoliation of graphite oxide into graphene oxide sheets, followed by reduction to GE nanosheets, and finally, the preparation of the GE/PVA nanocomposites by a simple solution-mixing method. The synthesized products were characterized by X-ray diffraction, field emission scanning electron microscopy, Fourier transform infrared spectroscopy, thermogravimetry, and differential scanning calorimetry analysis.

The GE nanosheets were well dispersed in the PVA matrix, and the restacking of the GE sheets was effectively prevented. Because of the strong interfacial interaction between PVA and GE, which mainly resulted from the hydrogen-bond interaction, together with the improvement in the PVA crystallinity, the mechanical properties and thermal stability of the nanocomposites were obviously improved. The tensile strength was increased from 23 MPa for PVA to 49.5 MPa for the nanocomposite with a 3.25 wt % GE loading. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 275–279, 2010

Key words: nanocomposites; mechanical properties; thermal properties

INTRODUCTION

Through the dispersal of strong, highly stiff fibers in a polymer matrix, high-performance lightweight composites can be developed.¹ However, there are many obstacles, such as the cost of nanoparticles, their availability, and the challenge of good dispersion.² Recently, graphene (GE) has attracted lots of interest in both the fundamental and applied fields because of its unusual physical, chemical, and mechanical properties.^{3–5} GE, as a new class of two-dimensional (2-D) carbon nanostructures, is a flat monolayer of graphite and is a basic building block for graphitic materials of all other dimensionalities.⁶ It is considered to be the thinnest and the strongest material to date.⁷ Although it was realized in 1991 that carbon nanotubes⁸ were formed by the rolling of a 2-D GE sheet, the isolation of GE was quite elusive, resisting any attempt on its experimental work until 2004. Geim et al.⁹ at Manchester University first isolated single-layer samples from graphite.¹⁰ Nowadays, GE can be obtained in large quantities

by the chemical reduction of graphene oxide (GO) with graphite as a raw material. Because graphite is cheap and readily available, this chemical approach is likely the least expensive and most effective method for the large-scale production of GE.

One possible route to harnessing these excellent properties of GE for applications would be to incorporate GE sheets in a composite material. It has been demonstrated that the incorporation of well-dispersed GE-based nanosheets into polymers can remarkably improve the properties of the polymer host materials.^{11–17} For example, Stankovich et al.¹¹ demonstrated that a polystyrene–GE composite exhibited a very low percolation threshold of about 0.1 vol % for room-temperature electrical conductivity, which reached about 0.1 S/m at only 1 vol % GE. Recently, Chen et al.¹² reported that when GO was incorporated into a poly(vinyl alcohol) (PVA) matrix, a 76% increase in the tensile strength and a 62% improvement in the Young's modulus was achieved by the addition of only 0.7 wt % GO. Therefore, GE/polymer composites are emerging as a class of exciting materials that hold promise for many applications. In this article, we report a simple and environmentally friendly method for the synthesis of GE/PVA nanocomposites by the incorporation of GE into a PVA matrix with water as the proceeding solvent. The as-synthesized GE/PVA nanocomposites showed improved thermal and mechanical properties.

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EXPERIMENTAL

Materials

Graphite was obtained from Qingdao Guyu Graphite Co., Ltd. (Qingdao, China), with a particle size of 150 μm . PVA (weight-average molecular weight = 1750 ± 50) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other reagents were analytical grade and were used without further purification.

Preparation of graphite oxide

Graphite oxide was synthesized from natural flake graphite by a modified Hummers method.¹³ In a typical procedure, natural flake graphite (1.0 g) was put into a 500-mL flask containing cooled (0°C) concentrated H_2SO_4 (40 mL). KMnO_4 (4.0 g) and NaNO_3 (1.0 g) were gradually added to the flask with stirring in an ice bath so that the temperature of the mixture was maintained below 15°C . The mixture was stirred at 35°C for about 1 h and then diluted with deionized (DI) water (80 mL). Because the addition of water to concentrated sulfuric acid medium released a large amount of heat, the addition of water was carried out in an ice bath to keep the temperature below 100°C . After all of the 80 mL of DI water was added, the mixture was stirred for 0.5 h and was then further diluted to approximately 350 mL with DI water. After that, 5% H_2O_2 was added to the mixture until the color of mixture changed to brilliant yellow. The oxidized suspension was washed with a dilute hydrochloric acid solution (5 wt %) to remove the sulfate ions and then centrifuged and washed with distilled water. The solid product was separated by centrifugation, and then, the suspension was dried in a vacuum oven at 60°C for 2 days to obtain graphite oxide.

Preparation of the GE aqueous dispersion

The graphite oxide powders (50 mg) were added to distilled water (50 mL) and then ultrasonicated for 1 h. The obtained brown dispersion was then subjected to 30 min of centrifugation at 3000 rpm to remove any unexfoliated graphite oxide. The result was a homogeneous dark brown dispersion of GO. In a typical procedure for the chemical conversion of GO to GE, the resulting homogeneous dispersion was mixed with 100 mL of water, 20.0 μL of hydrazine (75 wt %), and 150.0 μL of ammonia solution (28 wt % in water) in a 500-mL, round-bottom flask. The mixture was refluxed in an oil bath at 100°C under stirring for 5.0 h, over which the color of the solution gradually changed into dark black. The obtained dispersion was centrifuged for 15

min at 3000 rpm to remove a very small amount of precipitate.¹⁴

Preparation of the GE/PVA nanocomposites

The synthesis procedure for a typical GE/PVA nanocomposite with GE loading of 0.5 wt % was as follows: PVA (1 g) was dissolved in distilled water (10 mL) at 90°C , and the solution was subsequently cooled to room temperature. The obtained colloidal GE dispersion was gradually added to the PVA aqueous solution and sonicated for 1 h at room temperature. Finally, this homogeneous GE/PVA dispersion was poured into a culture dish and evaporated slowly in air to form a GE/PVA composite film, which was kept *in vacuo* at 60°C until the weight reached an equilibrium value. The thickness of the resulting film was about 30 μm . A series of GE/PVA nanocomposite films with different GE loadings were similarly prepared.

Characterization and measurements

The phases, structures, and morphologies of the as-synthesized products were characterized by X-ray diffraction (XRD; D/MAX-3C X-ray diffractometer) (Rigaku Corporation, Tokyo, Japan), transmission electron microscopy (TEM; Philips T20ST electron microscope at an acceleration voltage of 200 kV) (Amsterdam, Holland), and field emission scanning electron microscopy (JEOL JSM-7001F) (Tokyo, Japan). Fourier transform infrared (FTIR) spectra of the polymers were recorded on a Bruker 170SX FTIR spectrometer (Billerica, MA). The glass-transition temperature (T_g) and degree of crystallinity values of the samples were investigated by differential scanning calorimetry (DSC) with a PerkinElmer DSC-2C instrument (Waltham, MA). Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were carried out with a Netzsch STA449C thermal analyzer (Bavaria, Germany) under a protective nitrogen atmosphere (200 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$. The mechanical properties of the GE/PVA nanocomposites were measured by an electronic universal testing machine (KY8000A, Jiangdu Kaiyuan Testing Machine Co., Ltd., Jiangdu, China). All samples were cut into strips 50 mm \times 4 mm \times 30 μm with a razor blade. The tensile tests were performed in a controlled velocity of clamps of 50 mm/min.

RESULTS AND DISCUSSION

The FTIR spectra of the PVA and the GE/PVA composites are shown in Figure 1. In the IR spectrum of PVA [Fig. 1(a)], the characteristic bands assigned to methyl/methylene/methine ($\text{CH}_3/\text{CH}_2/\text{CH}$) stretch-

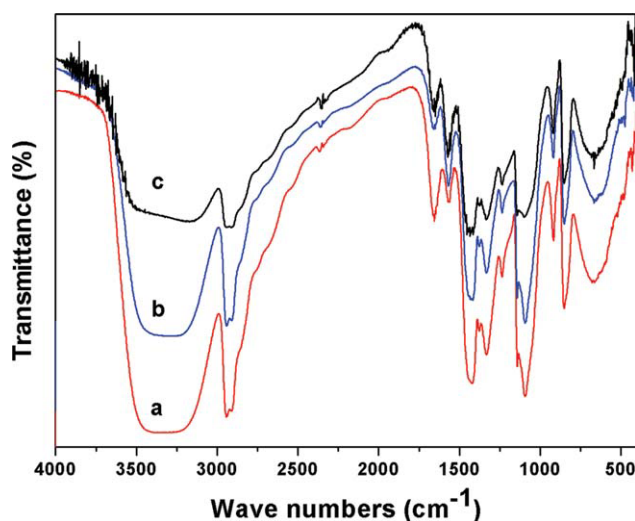


Figure 1 FTIR spectra of the (a) PVA film and GE/PVA nanocomposite films with GE contents of (b) 0.5 and (c) 1.3 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing and deformation vibrations were present in the 2800–3000- and 1300–1500- cm^{-1} ranges, respectively. The intense band at 3000–3600 cm^{-1} was due to hydroxyl groups in each polymeric unit.¹⁵ As shown in Figure 1(b,c), the GE/PVA nanocomposites showed similar IR spectra to pure PVA, and no obvious absorption peaks arising from GE were observed, which suggested a good reduction of GO. However, with increasing content of GE, the absorption bands of hydroxyl groups in the GE/PVA composites become wider; this indicated van der Waals forces and hydrogen-bond interactions between PVA and GE.¹⁵ It is generally recognized that GE nanosheets derived from the chemical reduction of GO still retain some hydroxyl, carboxyl, and other functional groups in their surface,^{16–18} which would facilitate their interaction with PVA.¹⁶

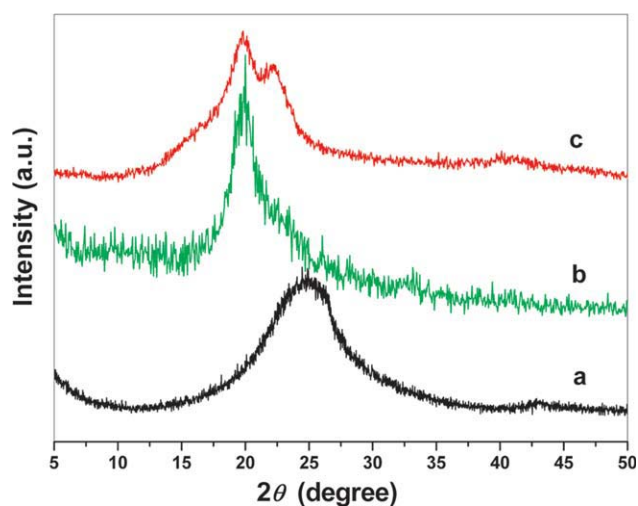


Figure 2 XRD patterns of the (a) GE nanosheets, (b) GE/PVA nanocomposite film (0.5 wt %), and (c) pure PVA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 2 shows the XRD powder patterns of the GE nanosheets, PVA, and GE/PVA nanocomposites, respectively. The GE nanosheets [Fig. 2(a)] showed a (002) diffraction peak at $2\theta = 24.8^\circ$, which corresponded to a d -spacing of 0.36 nm, which was slightly larger than that of graphite (0.34 nm; JCPDS no. 75-1621). Both the $d(002)$ value and the broadening of this reflection were typical for randomly ordered (turbostatic) graphitic platelets¹⁸ and were consistent with previous reports for GE nanosheets obtained from the chemical reduction of GO.¹⁹ Pure PVA [Fig. 2(c)] showed two strong diffraction peaks at $2\theta = 20$ and 22.1° and a weak diffraction peak around 40° , which were consistent with those reported in the literature.^{20,21} The GE/PVA nanocomposites [Fig. 2(b)] showed only a single diffraction peak around 20° , which should have arisen from PVA, and no diffraction peak from GE was observed. These results suggest that the orientation

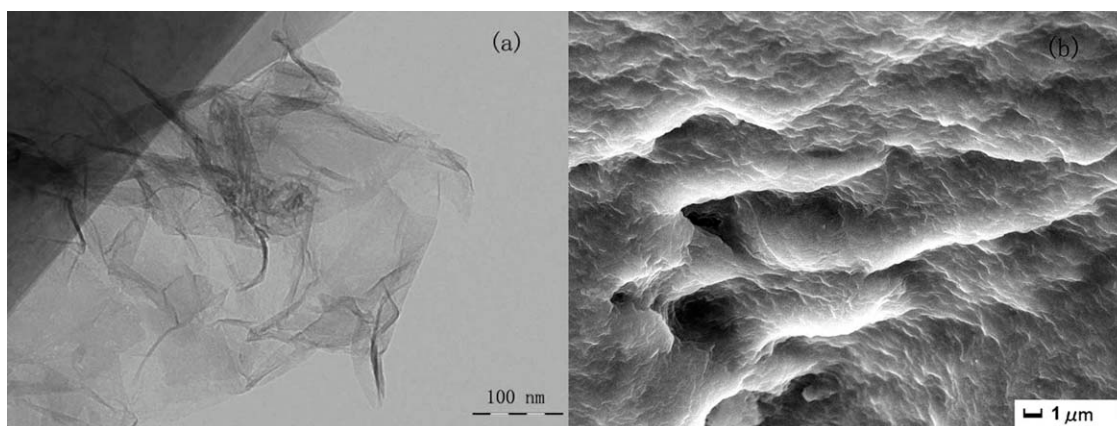


Figure 3 (a) TEM image of the GE nanosheets from an aqueous dispersion and (b) SEM cross-sectional image of the GE/PVA nanocomposite film (0.5 wt %).

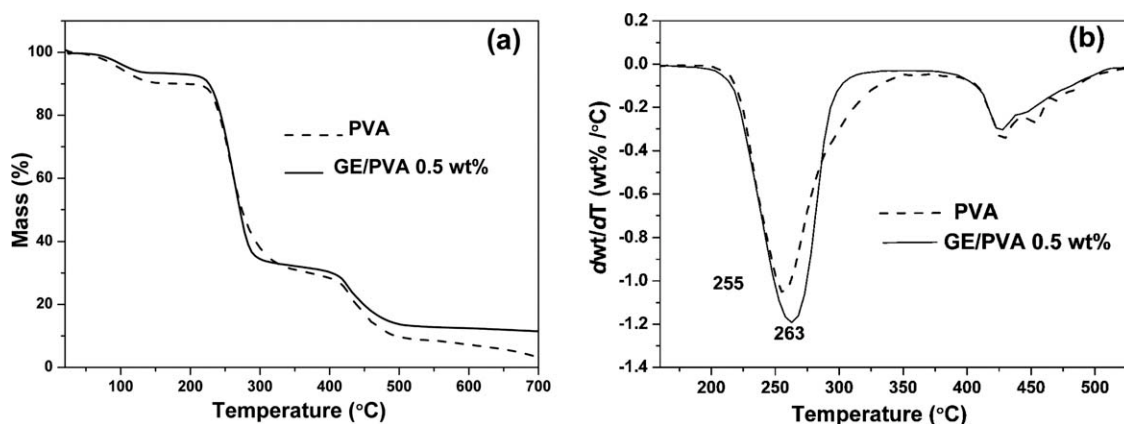


Figure 4 (a) TGA and (b) DTG curves of pure PVA and the GE/PVA nanocomposite (0.5 wt %). dwt/dT: 1st derivative of TGA curves.

of PVA in the composite was greatly improved, and the restacking of the as-reduced GE sheets was effectively prevented. Therefore, XRD patterns demonstrated a good dispersion of GE in the PVA matrix.

The morphology and structure of the as-synthesized products were further characterized by TEM and scanning electron microscopy (SEM). As shown in Figure 3(a), the GE nanosheets had a silklike appearance and were scrolled and entangled with each other. Corrugation and scrolling are part of the intrinsic nature of GE nanosheets, which result from the fact that the 2-D membrane structure becomes thermodynamically stable via bending.^{22,23} Therefore, GE nanosheets were successfully prepared via the exfoliation and reduction of GO. Figure 3(b) shows the cross-sectional SEM image of the GE/PVA nanocomposite film. The GE nanosheets were well dispersed in the PVA matrix. Because these wrinkled GE nanosheets were partially oxygenated, which would allow for enhanced interfacial interaction with polar polymer matrices, they may hold considerable potential as a new carbon-based nanofiller.

TGA was performed to investigate the effects of GE on the thermal stability of the polymer matrix. As shown in Figure 4(a), both PVA and its nanocomposite with a 0.5 wt % GE loading showed a

three-step weight loss process. The first step, a small weight loss occurring at about 60–150°C, was attributed to the loss of the residual (or absorbed) solvent. The second step, a big weight loss occurring at about 230–320°C, suggested the degradation of PVA. The third weight loss step, at about 400–500°C, should have resulted from the further decomposition of the remainders. The corresponding DTG is shown in Figure 4(b). The peak temperature of the DTG curve represented the temperature at which the maximum weight loss rate was reached. The peak temperature of the nanocomposite appeared at about 263°C and was increased by about 8°C compared to that of pure PVA. Although the increased value was lower than that of the functionalized GE sheets or expanded graphite-based polymer nanocomposites,² it was comparable to that of the GO/PVA nanocomposite with a 0.7 wt % GE loading.¹¹ These results indicate that addition of GE at low concentrations somewhat improved the thermal stability of the nanocomposite, which could be reasonably explained by the hydrogen-bonding interactions between the residual oxygen-containing groups of the GE sheets and the hydroxyl groups grafted onto the PVA backbone.²⁴ Because hydrogen-bonding interactions usually affect the mobility of PVA polymer chains and

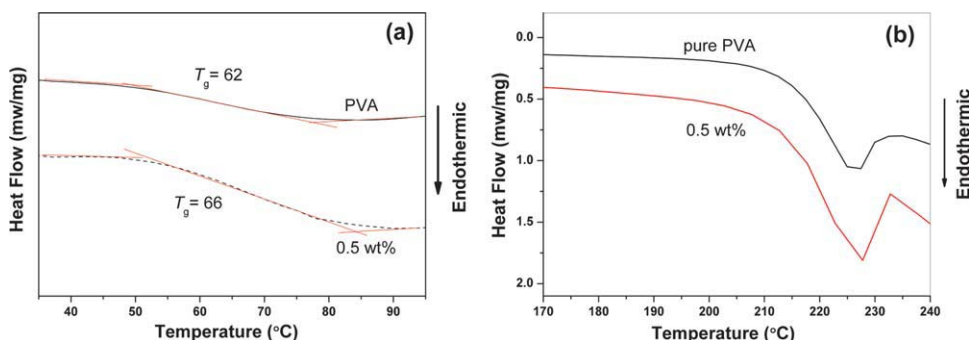


Figure 5 DSC curves of pure PVA and the GE/PVA nanocomposite (0.5 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

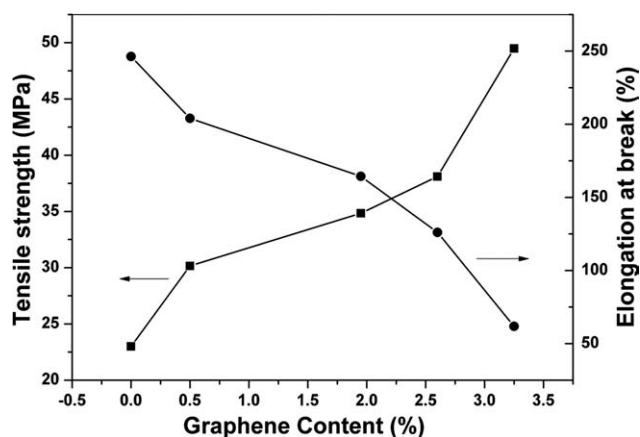


Figure 6 Mechanical properties of the GE/PVA nanocomposites.

because T_g is strongly dependent on the mobility of the polymer chains,²⁵ DSC analysis was used to compare the T_g of PVA with that of the GE/PVA nanocomposite. As shown in Figure 5(b), the T_g of PVA increased from 62 to 66°C for the GE/PVA nanocomposite with a 0.5 wt % GE loading. This T_g increase indicated that the polymer chains were indeed constrained by the hydrogen-bonding interaction. Furthermore, on the basis of the melting enthalpy [Fig. 5(b)], we found that the crystallinity of PVA in the GE/PVA nanocomposite was improved over that of pure PVA, probably because of the enhanced crystallization of PVA on the surface of the GE sheets.

The mechanical performance of the nanocomposites was expected to be significantly enhanced by the good dispersion of the GE sheets in the PVA matrix, strong interfacial adhesion due to hydrogen bonding between GE and PVA, and the improved crystallinity of PVA. As shown in Fig. 6, the mechanical performance of the GE/PVA composite film was significantly increased as compared to that of the pure PVA film. The tensile strength increased with increasing GE loading, from 23 MPa for PVA to 49.5 MPa for the nanocomposite with 3.25 wt % GE (Fig. 6). However, the breaking elongation of the nanocomposites decreased with increasing GE loading. When the amount of GE increased, the interaction between the GE sheets and PVA increased by van der Waals forces and hydrogen-bonding interactions; as a result, the movement of the PVA chains was seriously restricted. In addition, because PVA is semicrystalline, its mechanical performance strongly depended on the degree of crystallinity. As shown previously, the presence of GE resulted in an increase in the crystallinity of PVA in the GE/PVA nanocomposites. Therefore, the enhancement of the mechanical performance for the composites was attributed to the strong hydrogen-bonding interaction, improved crystallinity of PVA, and good dispersion of GE in the PVA matrix.

CONCLUSIONS

In conclusion, we demonstrated that GE/PVA nanocomposites could be fabricated with a simple and environmentally friendly water-solution processing method. The nanocomposites prepared by this procedure displayed interactions among the polymer and filler because of the remaining oxygenated groups in GE. The nanocomposites were superior to the pure polymer in their mechanical properties and thermal stability. The facile method presented here could be extended to the syntheses of other GE/polymer nanocomposites. Because of the abundant supply of graphite and the facile processability of functionalized GE sheets, GE as an effective nanofiller could be used for many practical nanocomposite applications.

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