

Polymer Communication

Facile preparation of epoxy-based composite with oriented graphite nanosheets

Weifeng Zhao, Haiquan Wang, Haitao Tang, Guohua Chen*

College of Material Science and Engineering, Huaqiao University, Fujian, Quanzhou 362021, China

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Abstract

A facile technique was built to fabricate epoxy-based composite film with graphite nanosheets (GN) alignment. GN were coated with magnetite nanoparticles and dispersed ultrasonically in epoxy resin. The homogeneous suspension was then cast on a poly(tetrafluoroethylene) substrate and subjected to an external unidirectional magnetic field before the mixture got solidified. X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements showed that the modified GN embedded in epoxy resin were aligned along the magnetic field direction, which was perpendicular to the film plane. The transmittances of the film samples, measured by UV–visible spectrometer, were improved due to the orientation of the GN fillers.

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1. Introduction

Polymer/GN composites have attracted lots of attentions recently [1–9]. By blending polymer with expanded graphite (EG), one can achieve GN-reinforced polymer nanocomposites with electrical conducting percolation thresholds as low as 1.0–5.0 wt%, much lower than those filled with pristine graphite powder. The GN dispersed in the polymer matrix are usually 10–80 nm in thickness. More recently, Chen et al. [10,11] sonicated the expanded graphite in alcoholic solution and obtained individual GN with an average thickness of about 50 nm and a diameter of 5–20 μm . The polymer/graphite nanocomposites can be prepared by adding the GN powder instead of EG into polymer matrix. The dispersion of GN in the polymer matrix can be effectively enhanced with the help of ultrasonication or other mixing methods. Several GN composites have been prepared and investigated such as PA6/GN, PS/GN, PMMA/GN, UP/GN by Chen's group

[11–15]. Composites of PANI/GN, poly(arylene disulfide)/GN [16,17], NBR/GN [18], and PMMA/Ce(OH)₃, Pr₂O₃/GN [19] have been reported by other groups. These studies show that the high aspect ratio of the isolated GN makes them satisfy the percolation transition of conductivity at a remarkably low volume fraction in the polymer matrix. Merely recently, we have found that GN tend to align in polymer matrix, resulting in the polymer-based nanocomposites with unique piezoresistivity [20] (positive pressure coefficient, PPC) and positive temperature coefficient (PTC) properties [13]. Actually, not only electrical conductivity but also tensile strength, modulus and anisotropic properties of the polymer/GN composites are linked directly to the orientation of the GN. In light of the ordering of GN intimately correlates with these remarkable properties, we realize that it is important to align GN in the polymer matrix purposefully. Many papers in the literatures [21–26] have reported the alignment of layered silicates and carbon nanotubes in the polymers, while the efficient ordering of this new GN conducting filler seems to be a virgin field. Presently, several techniques have been proposed to align the carbon nanotubes in the polymer matrix, including magnetic

* Corresponding author. Tel.: +86 595 22692956; fax: +86 595 22686969.
E-mail address: hdcgh@hqu.edu.cn (G. Chen).

field, electric field, and shear-force. In this article, a magnetic-induced approach is presented for the preparation of polymer-based composites with GN of ordered alignment. GN were first coated with magnetite nanoparticles, and dispersed in epoxy pre-polymer, and finally induced to align by magnetic force before the suspension was crosslinked.

2. Experimental section

2.1. Materials

GN used here were prepared by the ultrasonic techniques from pristine graphite which were detailed in Ref. [10]. Epoxy resin, diglycidyl ether of bisphenol-A (epoxy equivalent weight (EEW) ≈ 227 , $\rho = 1.18 \text{ g/cm}^3$, softening point: 12–20 °C), was supplied by Ruida Chemical Factory (China). All the reagents (analytical pure) below were commercially available. Ethanol, iron(III) chloride hexahydrate, iron(II) sulfate heptahydrate, sodium hydroxide, and ethylenediamine (EDA) used as hardener were obtained from Shantou Xilong Chemical Factory (China).

2.2. Magnetic functionalization of GN

The as-prepared GN were magnetically modified by the wet-chemical coprecipitation of magnetite nanoparticles on their surfaces. GN (1.00 g) were dispersed ultrasonically with 50 mL aqueous $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.01 mol/L) solution and 50.00 mL aqueous $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (0.05 mol/L) in an ultrasonic bath with water as the coupling fluid at 30 °C for 30 min. The mixture was transferred into a water bath at 30 °C and was given a continuous agitation. Aqueous NaOH solution (0.40 mol/L) was added continuously until the pH of system reached 12 during the stirring process. The final mixture was stirred for an additional 10 min and then kept in a water bath at 50 °C for 2 h. Finally, the product was filtered and washed with double distilled water several times until it got neutral and then allowed to dry under vacuum into powder. The obtained powder as filler, in which coated GN and a small quantity of free magnetite particles coexisted, was used without further treatment.

2.3. Preparation of ordered composite film of epoxy/GN

The acetone diluting epoxy resin (10.00 g epoxy resin with 1.50 mL acetone) with the addition of 0.45 g as-prepared filler was ultrasonicated in a water bath at the temperature of 50 °C for about 1 h to obtain homogeneous dispersion of GN. After adding 0.80 g of ethylenediamine (EDA), the mixture was stirred mechanically for 5 min. The suspension was casted on a poly(tetrafluoroethylene) substrate, and the sample was subjected to a constant magnetic field of 800 T at 30 °C till cross-linking of the sample, thus making a film with a thickness of approximately 0.1 mm, as shown in Fig. 1.

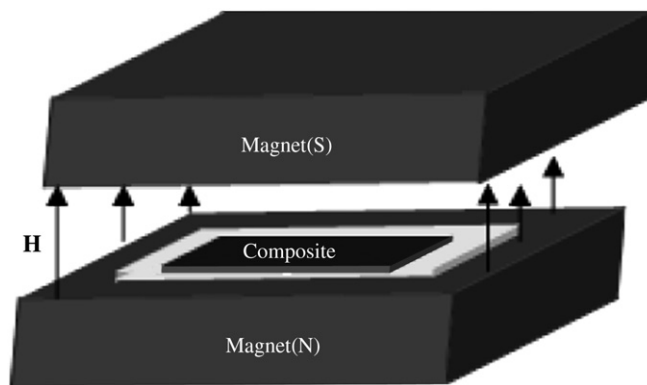


Fig. 1. Schematic illustration of magnetic field-inducement on an epoxy/GN sample.

2.4. Measurement

Electron microscopy studies were carried out with LEO 1530 field-emitting scanning electron microscopy (Germany) at the operating voltage of 20 kV for the observation of surface morphologies of the magnetically modified GN filler.

X-ray diffraction and atomic force microscopy (AFM) were employed to demonstrate the orientation of the GN in solidified epoxy resin. X-ray diffractometer of D8-Advance supplied by Germany was used to scan the composite film from 10° to 31° at a rate of 2° per min. $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$), the X-ray source, was generated at the voltage of 40 kV and a current of 40 mA. AFM image was obtained on a VEECO/DI-CP-2 scanning probe microscope. The phase image was acquired.

Samples were cut into square with typical dimensions of $50 \times 12 \times 0.1 \text{ mm}^3$ for transmittance measurement of the composites. The transmittance was recorded by a UV–visible spectrophotometer (UV-1600, China) at room temperature in 400–750 nm region across the thinnest direction along the direction of magnetic field.

3. Results and discussions

3.1. Magnetic modification of GN

The obtained filler was a mixture of coated GN and magnetite particles resulted from the coprecipitation treatment. However, the free magnetite particle, which was of small amount, was proved to be adiphorous to the succeeding orientation of coated GN in the epoxy matrix.

Fig. 2 is the typical SEM images of GN before and after modification. Fig. 2(a) shows the sheet-like feature of GN before modification with smooth surface and high aspect ratio. The individual nanosheets have a diameter of a few micrometers. Their thickness is 20–60 nm. Fig. 2(b) reveals the GN coated by magnetite nanoparticles. The size of nanoparticles ranges 10–20 nm and the particles distribute over the surface of GN quite widely and homogeneously.

The interaction between nanoparticles and GN appeared so strong that even intensive sonication could not remove the

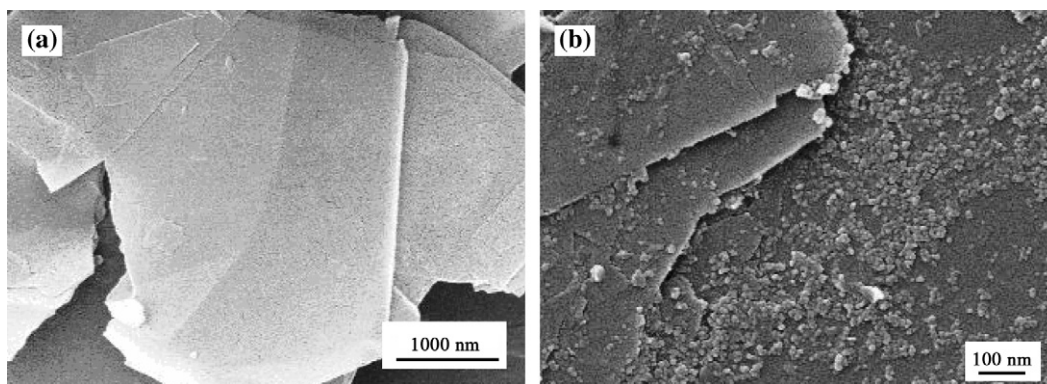


Fig. 2. SEM micrographs of GN before (a) and after (b) modification.

nanoparticles from the GN surfaces. The strong attachment of magnetite nanoparticles onto the surface of GN is mainly due to the powerful inter-attracting magnetostatic force between the nanomagnetite coats onto the both sides of each graphite nanosheet; the coated GN powder appeared a saturation magnetization (M_s) of 30 emu/g and 470 Oe of coercive force (Vibrating Sample Magnetometer (QD PPMS-9T, USA)) at room temperature [27]. Details [27] will be presented in further publication. These magnetic nanoparticles endowed the GN with magnetic property, so that the modified GN could be attracted and even picked up by a normal bar magnet, while the unmodified GN were inert under normal magnetic field.

3.2. The orientation of GN in epoxy matrix

The pre-polymeric system for the preparation of composite film consisted of epoxy resin, coated GN, a small amount of residual acetone, curing agent and a spot of free magnetite particles. As the pre-polymeric mixture was subjected to the unidirectional magnetic field, the modified GN were favorable to turn to minimize the magnetostatic energy and overcome free energy (Brownian motion) of the system, and reorient themselves into a stable configuration. Oriented GN were frozen by the polymerization of the epoxy pre-polymer, leading to an epoxy/GN ordered composite film.

The reorientation of GN in the pre-polymeric medium was restrained by the viscous shear arising from the polymer chains and by the encumbrances of GN themselves relating with their concentration. High fraction of acetone could retard the curing rate of epoxy resin. To solve these problems we diluted the viscous epoxy resin with acetone and ultrasonicated the mixture of diluting epoxy resin/coated GN at a high temperature (50 °C). This procedure promoted the distribution of GN as well as evaporated a certain amount of acetone to ensure a GN suspension with proper viscosity for both the reorientation of GN and curing of the pre-polymeric host.

The orientation of GN inside the epoxy matrix was evidenced by X-ray diffractions. Fig. 3a displays that the composite sample without magnetic field-inducement shows a strong peak at $2\theta = 26.4^\circ$, which is due to the scanning from 002 planes of GN. This sharp peak becomes very weak on the curve of magnetically induced specimen (Fig. 3b). This change

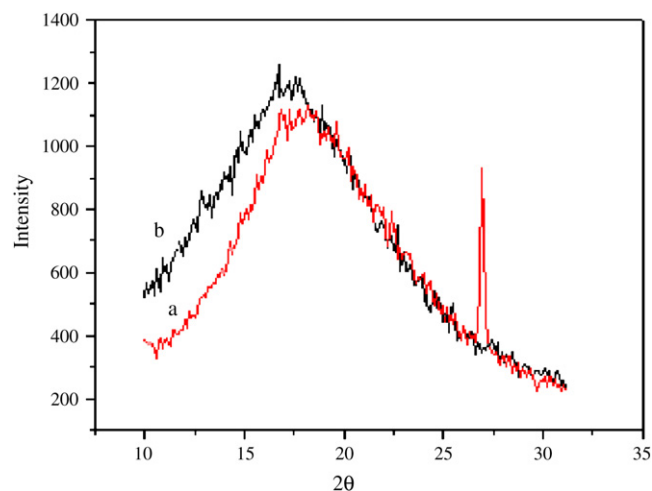


Fig. 3. XRD patterns of epoxy/GN composites without (a) and with (b) application of magnetic field.

indicates that GN have been magnetically induced to align in the magnetic field direction with their hexagonal planes perpendicular to the sample surface. It is understood that when all (or subtotal) graphitic crystallites reoriented in the direction perpendicular to the film plane, it will cause the absence of regular planes that satisfy the Bragg's equation $2d \sin \theta = n\lambda$ at $2\theta = 26.400^\circ$, resulting in the disappearance of the significant diffraction peak on the X-ray pattern [28].

The morphology of the oriented GN in matrix was also verified by AFM [26,29]. Fig. 4 shows the AFM phase image of film surface of magnetic field-induced sample. Sticks of 30–50 nm in width and several micrometers in length are the GN in their thickness direction, which indicate that GN platelets embedding in the epoxy matrix are perpendicular to the composite film surface. The AFM image also shows a well dispersion of GN within epoxy matrix.

3.3. The properties

The anisotropic structure may be the most interesting feature for the as-prepared epoxy/GN film. Fig. 5 shows the different transmittances in the wavelength region of 400–750 nm between the field-induced (a) and chaotic composite (b) films.

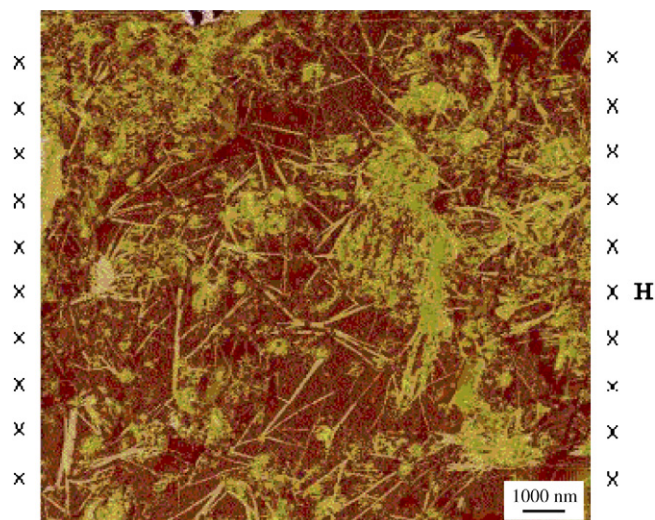


Fig. 4. Atomic force microscopy of the top view of induced composite film. The direction of magnetic field is perpendicular to the plane of image.

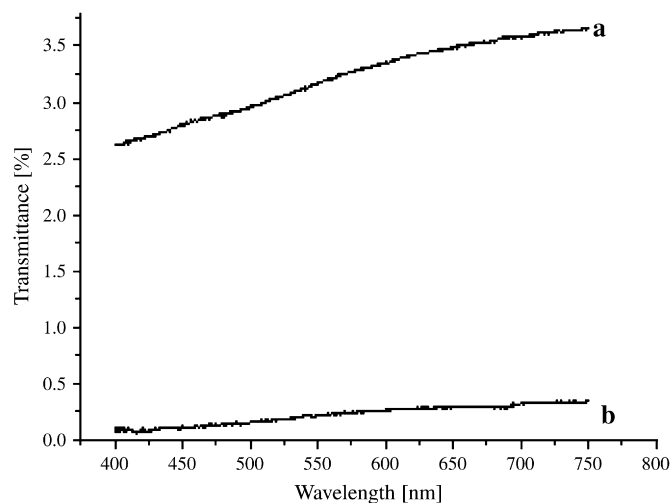


Fig. 5. The transmittances of the ordered (a) and chaotic composite films (b) with filler content of 4.3 wt%.

It shows that the transmittances of the field-induced film sample are significantly improved in the visible light region. This is another evidence of the orientation of GN in epoxy matrix. When the GN lamellas are aligned perpendicular to the film plane, the area of obstacles to the light transmitting

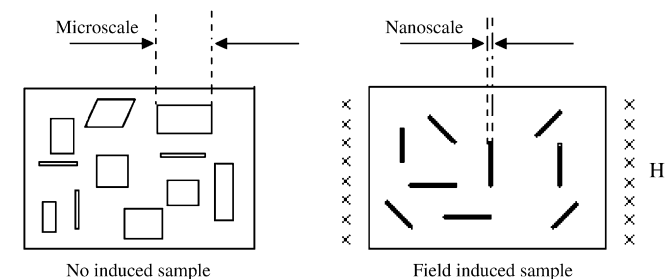


Fig. 6. Schematic illustration for the reason of the improvement in light transmittance.

is minimized along the orientation direction, leading to a broader window for the light transmitting, which is illustrated in Fig. 6.

4. Conclusions

Epoxy-based composite films with oriented GN coated with magnetite nanoparticles were prepared under magnetic field. XRD and AFM measurements showed that GN were successfully reoriented along the magnetic field direction that was perpendicular to the film plane. The orientation of GN, sheet-like filler, brought about an improvement in transmittance of the composites in the wavelength region of 400–750 nm. Further works will be focused on the investigation of anisotropic properties of the composite.

Acknowledgements

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