Preparation of polymer/oriented graphite nanosheet composite by electric field-inducement

Haiquan Wang, Hongyan Zhang, Weifeng Zhao, Wei Zhang, Guohua Chen *

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

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Abstract

Graphite nanosheets (GNs) prepared by sonicating expanded graphite were homogeneously dispersed in unsaturated polyester resin using sonication. The dispersion with a curing agent was then subjected to a dc electric field, followed by crosslinking, to fabricate a polymer/GN composite film. X-ray diffraction and scanning electron microscopy revealed that the GNs in the film were oriented parallel to the electric field. UV–VIS measurements indicated that the optical properties of the field-induced composite film showed significant improvement in visible light transmittance compared with those prepared without the electric field.

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1. Introduction

Graphite nanosheets (GNs) are considered as highly prospective filler materials for future polymer composites due to the high aspect ratio and superior electrical and thermal conductivity. They have thicknesses in the nanometer scale, and up to several microns in diameter. Recently, there has been an increased interest in composites of GNs and polymers [1–9]. Celzard et al. [10] firstly investigated the conductive behavior of 100 µm-thick composite films composed of epoxy resin and expanded graphite flakes with an average diameter of 10 µm and an average thickness of 100 nm. It was only 1.3 vol% graphite sheet that was needed to reach the percolation threshold. Recently, Chen et al. [11,12] proposed fragment of expanded graphite by ultrasonic irradiation without grinding. The thickness of the foliated graphite varied from 10 to 100 nm, and the aspect ratio is as high as 100–300. The foliated graphite nanosheets were successfully incorporated into polystyrene [12], Poly(methyl methacrylate) [13], nylon6 [14], unsaturated polyester resin [15] to fabricate nanocomposites with very low values of percolation threshold. Merely recently, we found graphite nanosheets tend to align in the polymer matrix under shear force, and the received nanocomposite has unique piezoresistivity [16]. Many literatures [17–29] have reported the alignment and assembly of particles, carbon nanotubes, and nanofibers, whereas there are very few reports on the orientation and alignment of conductive nanosheets. Because of the high aspect ratio and the flake-like shape of the GNs, unique properties are expected for the GNs-polymer composites when the GNs are oriented in a certain direction. Herein, we describe a strategy that orients the GNs in one direction in the unsaturated polyester resin by the electric field. The electric field is applied by two parallel electrodes and the electric field-induced torque is the driving force for the orientation of the GNs. SEM and XRD techniques have been applied to demonstrate the orientation of the GNs. In addition, the optical properties of the composite have been investigated within the visible wavelength (400–750 nm).
2. Experimental

2.1. Materials

The unsaturated polyester resin used in this study was supplied by Quanzhou Unsaturated Polyester Resins Factory (Quanzhou, China). Methyl ethyl ketone peroxide 1 wt% and cobalt octoate 2 wt% were used as the initiator and accelerator, respectively. The fillers used were GNs prepared by the ultrasonic techniques from nature graphite which has been detailed in [12]. These GNs have a size of 10–80 nm in thickness and 5–20 μm in diameter.

2.2. Preparation of oriented unsaturated polyester resin/GN films

Preweighed unsaturated polyester resin and GNs were mixed together and sonicated for 20 min to randomly disperse the inclusions. Afterwards 1 wt% accelerator and 2 wt% initiator were added and dispersed by conventional stirring. Then cast the suspension into the setup and apply the electric field till complete crosslink of the matrix. The concentration of GNs was varied from 0.1 wt% to 1.3 wt%. The dc electric field was applied using parallel electrodes which were fabricated by etching indium-tin-oxide (ITO) onto a glass substrate. Fig. 1 illustrates the experimental setups used to apply a dc field. The dc electric field was fixed at 18 V and supplied by typical dc voltage equipment (YJ26G, China). The gap between the electrodes was 0.20 mm, so 90 V/mm was applied to the dispersion. Under this condition, the matrix will cure in a few minutes.

2.3. Characterization and measurements

The aforementioned sample removed from the electric field was immersed into the saturated NaOH/alcohol solution for 2 h to erode the polymer matrix around the GNs. In the NaOH/alcohol solution, the matrix was etched for the alcoholysis and the GNs were exposed. The eroded GNs in the matrix were observed with a LEO-1530 field-emitting scanning electron microscope to examine the morphology of GNs in the matrix.

Removal of the glass electrodes left a smooth, glossy surface suitable for spectrophotometric analysis. The films were cut into rectangular samples with dimensions of 40 × 12 × 0.2 mm for transmittance measurements, and into round samples with diameters of 27 mm for reflectance measurements. The reflectance and transmittance of the films were acquired via a UV–VIS–NIR 3100 recording spectrophotometer over the range of visible wavelength (400–700 nm).

X-ray diffraction was employed to demonstrate the orientation of the GNs in the unsaturated resin. X-ray diffractometer of D8-Advance supplied by Germany was used to scan the composite sample from 10° to 40° at a rate of 2°/min. CuKα (λ = 0.15405 nm) radiation that was generated at the voltage of 40 KV and a current of 40 mA was used as the X-ray source.

3. Results and discussion

3.1. The orientation of GNs in unsaturated polyester resin

Applying an electric field to the dispersion of the graphite nanosheets in liquid unsaturated polyester resin induces the orientation of GNs from a random state. Either alternating current (ac) or direct current (dc) electric fields can be used to orient the GNs whose electric properties differ from those of the suspending matrix.

In the presence of an electric field, the GNs undergo a polarization. For the GNs having crystalline anisotropy, the polarization moment μ is generally not aligned with the electric field E, and this polarization can be divided into two contributing components, i.e., one parallel to the flake (μ∥) and one perpendicular to the flake (μ⊥). For GNs, the polarization parallel to the flake is much larger than that perpendicular to the flake. μ⊥ and μ∥ are given as [30]

\[
\mu_\parallel = \varepsilon_0 \varepsilon_2 \left( \frac{\sigma_1 - \sigma_2}{\sigma_1} \right) V E \cos \theta, \tag{1}
\]

\[
\mu_\perp = \varepsilon_0 \varepsilon_2 \left( \frac{\sigma_1 - \sigma_2}{\sigma_1} \right) V E \sin \theta, \tag{2}
\]

where \( V \) is the revised volume of a single GN, \( \theta \) is the angle between the direction of the dc electric field and the flake axis. \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_2 \) is the relative dielectric constant of the resin matrix, \( \sigma_1 \) and \( \sigma_2 \) are the conductivity of the GN and resin matrix, respectively. An illustration of the behavior of a flake exposed to a uniform electric field is given in Fig. 2.

This polarization leads to a field-induced torque \( T \) acting on the flake which is given by \( T = \mu \times E \). Because the polarization moment \( \mu \) is not codirected with the electric field \( E \), the resulting field-induced torque \( T \) is not zero. The GNs have shape anisotropy due to the flake-like shape, so the polarization moment \( \mu \) cannot be aligned to the electric field \( E \). The overall torque acting on the GN can be superposition of torques due to fields which are parallel and perpendicular to its axis. \( T = \mu_\parallel \times E_\parallel - \mu_\perp \times E_\perp \) (where \( E_\parallel = E \cdot \cos \theta \) and \( E_\perp = E \cdot \sin \theta \)). The field-induced torque acting on the GN is [30]...
Under the given conditions, this torque orients the GN against the viscous drag of the resin matrix in the direction of the electric field.

SEM was employed to examine the morphology of the UR/GN composite. Fig. 3 shows the scanning electron microscopy image of an oriented composite film surface etched by saturated NaOH/alcohol solution. We can see that the GNs were oriented with their flakes perpendicular to the film surface, in other words, parallel to the direction of the electric field. In contrast, Kim [17] has achieved aligned chain-like structures of graphite particles in the epoxy under a 5 Hz and 1.2 kV/mm electric field. Compared with the sphere-shaped graphite particles, graphite nanosheets were oriented in a different structure in the matrix under the electric field. Moreover, graphite nanosheets were oriented under a lower electric field due to the unique two-dimensional flake-like shape and high aspect ratio.

The electric field-induced orientation process of GNs mentioned above can be proved by the large pristine graphite. It has been confirmed that both graphite nanosheets and original graphite were composed of basic elements of graphite layers; no gallery space change occurs during manufacture [11]. Therefore, the mechanism of GNS’ orientation in un-crosslinked thermosetting resin is applicable in the case of graphite flake of large scale. The electric field-

![Fig. 2. Schematic illustration of a polarized flake in an electric field.](image)

![Fig. 3. Scanning electron microscopy image of an oriented UR/GN composite containing 0.974 wt% GN.](image)

![Fig. 4. Optical observation of graphite flakes (0.2 wt%) in unsaturated polyester without electric field-inducement (a), with field inducement in the direction parallel to the observation (b) and perpendicular to the observation (c).](image)

![Fig. 5. Schematic illustration of electric field-induced orientation of the GNS in unsaturated resin. (a) the initial random state (b) the oriented state.](image)
inducement of GNs could be attested by the orientation of graphite flake with larger diameter (0.3–0.5 mm). Without the electric field, the graphite flakes were randomly dispersed in the suspension as shown in Fig. 4a. After the application of the electric field, the graphite flakes were rapidly rotated and orientated along the direction of the electric field within 30 s as observed in Fig. 4b. The dotted lines in Fig. 4b demonstrate the orientation of graphite flakes through polarization. It was observed that the concentration of graphite flakes did not vary with distance from either the anode or cathode. Electrophoresis was not visible during the experiments during the graphite orientation.

Figs. 5 and 6 illustrate the mechanism for the orientation of the GNs. At the beginning, the GNs were randomly dispersed in the resin matrix (Figs. 5a and 6a). Induced by the electric field, the GNs were oriented with their flakes along the electric flux (Figs. 5b and 6b).

A sharp decrease in the diffraction maximum at $2\theta = 26.4^\circ$ of Fig. 7a shows that the electric field has oriented the GNs with their planes parallel to the normal axis of the sample surface. The strong peak at $2\theta = 26.4^\circ$ of Fig. 7b is resulted from the diffraction of (002) planes of the graphite. It is understood that when all graphitic crystallites were oriented in the direction parallel to the normal axis of the film plane, it will cause the absence of regular planes that satisfy the Bragg’s equation $2d \sin \theta = n\lambda$ at $2\theta = 26.4^\circ$, leading to the disappearance of the significant diffraction peak on the X-ray pattern.

### 3.2. Optical properties

The structural anisotropy of composites containing oriented fillers often results in anisotropic properties. When the GNs with high aspect ratio were oriented by the electric field, it must result in variations of optical properties, such as light transmittance, light absorbance, and diffuse reflectance, etc. At low weight fraction of the GNs, the composite is somewhat translucent. The optics of translucent material has been studied theoretically by Kubelka and Munk [31]. The Kubelka–Munk theory provides a reflectance model for translucent materials placed on backings of different colors, and the Kubelka–Munk equations model the light scattering and absorption within translucent materials. This model ignores the internal and external reflections at surface or interface. A fluid of the same refractive index as that of the cured resin was used between the sample and the backing to eliminate the internal reflection. These reflections needed to be corrected before applying the model [32].
Fig. 8 shows the transmission optical photographs of UR/GN composite films. Apparently from the figure, the letters can easily be seen through the oriented composite. However, the letters are obscure if seen through the random composite. It illustrates that the transmittance of the oriented composite film was significantly improved due to the orientation of the GNs. The same result was received in the same experiments without adding curing agent. So we can deduce that the different level of curing is not the reason that causes the change in transmittance. Under the electric field, the graphite nanosheets were oriented rapidly, and the monomer was cured in a few minutes. The electrophoresis did not occur in the experiment, so electrophoretic migration is not the reason for the improvement for the transmittance.

Transmittance as function of wavelength is plotted in Fig. 9 for each of the composite films. Fig. 9 shows that the transmittance of the oriented composite film is significantly improved in the range of visible wavelength (400–750 nm). When the GNs were oriented with their flakes parallel to normal axis of the film plane, the light is likely to encounter less resistance due to the high aspect ratio of the GNs, leading to the improvement of transmittance, which is illustrated in Fig. 11.

At low weight fraction of the GNs, the composites are translucent, so their diffuse reflectances are dependent on the backing according to the Kubelka–Munk theory. Fig. 10 shows that the ordering of the reflectance curves with the white backing (oriented > randomly) was the reverse of the ordering of the reflectance curves with the black backing (randomly > oriented). According to the Kubelka–Munk theory, the backing plays an important role in the diffuse reflectance of the translucent materials, so the change of ranking is easily understood. The composites that are oriented parallel to the light flux absorb and scatter less light than the composites that are randomly dispersed due to the high aspect ratio of the GNs. It is well known that large particles tend to absorb and scatter more light than small particles due to the larger surface area. When oriented with their flakes along the light flux, the GNs may have optical properties similar to the small particles, and the randomly dispersed GNs may have optical properties similar to the large particles, which is illustrated in Fig. 11. The oriented composite is brighter than randomly dispersed composite on the white backing because it absorbed less amount of the light. The randomly
dispersed composite is brighter than oriented composite on the black backing because it scattered more light to the observer.

4. Conclusion

In summary, it was successfully demonstrated that the GN were oriented with their flakes along the electric flux under the influence of an dc electric field. The optical properties of the field-induced composite films showed significant improvement in visible light transmittance compared with those prepared without the electric field within the visible wavelength range. The oriented composite film tended to absorb and scatter less light than the random one.

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References
