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# Self-orientation of graphite-nanoplates induces anisotropy of nanoplates-epoxy composites

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## Abstract

Graphite nanoplates-epoxy composites with anisotropic dielectric properties were prepared via a solution route. The self-orientation of the graphite nanoplates in the epoxy matrix leads to the anisotropy of the composites. The dielectric permittivity in the direction parallel to the surfaces of the samples is about several times of that perpendicular to their surfaces. The out-of-plane dielectric permittivity of the 1.2 wt.% graphite nanoplates-epoxy composite is 8 at 1 MHz, while the in-plane dielectric permittivity is 39. The dielectric loss in both directions is below 0.05. High dielectric permittivity and low dielectric loss of the composites make them have potential applications in embedded capacitors.

*Keywords:* B. Composites; Dielectric permittivity; Graphite nanoplates; Self-orientation

## 1. Introduction

Graphite nanoplates (GNs) have been widely investigated in recent years, for their good electrical and thermal conductivity [1–4]. They have unique layered structure with large aspect ratio, e.g., with thickness of nanometer scale and diameter of up to several microns. Several methods have been employed to prepare GNs, such as conversion of nanodiamond [5], arc evaporation of SiC [6], reductive pyrolysis of camphor [7] and exfoliation of graphite oxide [8]. Among them, the method of exfoliating graphite oxide is more convenient for preparation of masses of GNs, which provides possibility for GNs to be used in composites.

High-dielectric constant (high-k) polymer-based composites with low dielectric loss for embedded capacitors and high density energy storage are in pressing need to further miniaturize electronic systems and enhance performance of them. Although polymer composites containing high-k ceramic particles could fulfil the basic requirement of moderate dielectric permittivity and low dielectric loss [9], the high load of ceramic particles in the composites presents a number of limitations, in terms of high weight, low flexibility and poor mechanical performance [2,10]. To overcome these disadvantages of such ceramics–polymer composites, conductive fillers are chosen to fabricate high-k polymer-based composites in terms of percolation theory [10,11].

GNs can be selected as a species of conductive fillers, since their unique layered structure with large aspect ratio can assure a very low filler loading of GNs in the composites [1,3]. Layered structure may lead to the composites anisotropic properties, if GNs are not randomly oriented in the composites. For example, Zhao et al. [12] prepared epoxy-based composite films containing oriented GNs coated with magnetite nanoparticles under magnetic field, which led to an improvement in transmittance of the composites in the wavelength region from 400 nm to 750 nm. Wang et al. [13] prepared polymer/oriented GNs composite induced by applying a large electric field, which tended to absorb and scatter less light than random one. Actually, due to their unique layered structure with large aspect ratio, GNs could tend to self-orientate in the fluid polymer matrix under the tension of the liquid without external magnetic or electric field. In this article, we prepare polymer-based composites with self-orientated GNs as conductive fillers via a solution route. These composites present obvious anisotropic properties. The proper dielectric permittivity and low dielectric loss of the composites make them have potential applications in embedded capacitors.

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## 2. Experimental

Natural flake graphite (Qingdao Tiansheng Graphite Company) was used as the starting material to produce GNs by chemical exfoliation. The mixture of 3 g natural graphite, 30 ml $H_2SO_4$ and 90 ml $HNO_3$ was stirred for 6 h to prepare graphite oxide. The graphite oxide was then filtered from the acid solution, washed by deionized water and ethanol, and finally dried at 120 °C for 8 h. The dried graphite oxide powder was then heated at 1050 °C for 10 s by a rapid thermal annealing oven to obtain thermally expanded graphite oxide. GNs were ready for use after the thermally-expanded graphite oxide was dispersed in acetone for 2 h by ultrasonic exfoliation.

Stable suspension of the GNs in acetone solution was prepared by ultrasonic exfoliation. E44-epoxy resin (WRS 6101, Wuxi Resin Factory) with various weights was added to the stable suspension and dissolved by stirring. Then the mixture was heated to 80 °C and kept for 3 h to remove the solvent. Diethylenetriamine was then added to the mixture as the curing agent. The final mixtures with different weight percentages of GNs were cured for 24 h in the air at room temperature in rectangular molds with the size of 20 mm × 20 mm × 2 mm. Silver electrodes were painted on both sides of the samples. Fig. 1 shows the schematic of the composite samples. A-face is the top surface of the sample. The out-of-plane direction is perpendicular to the A-face, and the in-plane direction is parallel to the A-face.

Transmission electron microscopy (TEM, JEOL2011) was used to observe the exfoliated GNs. Dielectric properties, along the out-of-plane direction and the in-plane direction, were measured by employing a HP 4194A impedance analyzer in the frequency range from 1 kHz to 40 MHz at room temperature.

## 3. Results and discussion

Typical TEM micrographs of exfoliated GNs used in the composites are shown in Fig. 2. The size of the GN is about 20 μm in side width and about 5 nm in thickness, with a large aspect ratio of over 1000. Fig. 3 shows the distribution of the GNs in the epoxy matrix. As seen from Fig. 3(a), the surface micrograph of the 1.2 wt.% GNs-epoxy composite sample shows that the GNs are dispersed into the epoxy matrix without serious aggregation. Moreover, most of the GNs lie parallel to the sample surface, illustrating obvious self-orientation. But much differently from Fig. 3(a), not surface but side edges of the GNs are seen in the B-face of the sample as shown in Fig. 3(b). Low density of carbon, large specific surface, and proper viscosity of the resin matrix enable the stable suspension of the GNs in the matrix during the curing process, which ensures the homogeneity of the composites. Thus the side edges of the GNs are uniformly distributed in the B-face. From the distribution of the side edges, the self-orientation of the GNs

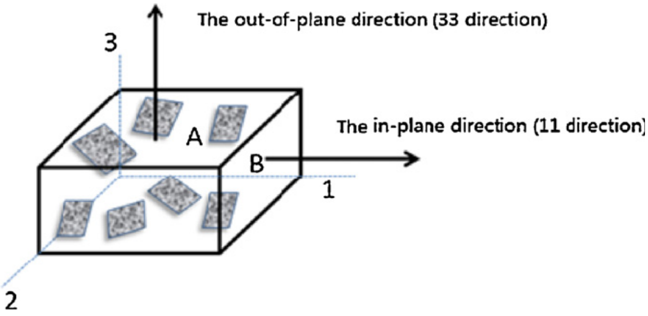

Fig. 1. Schematic of the GNs-epoxy composites.

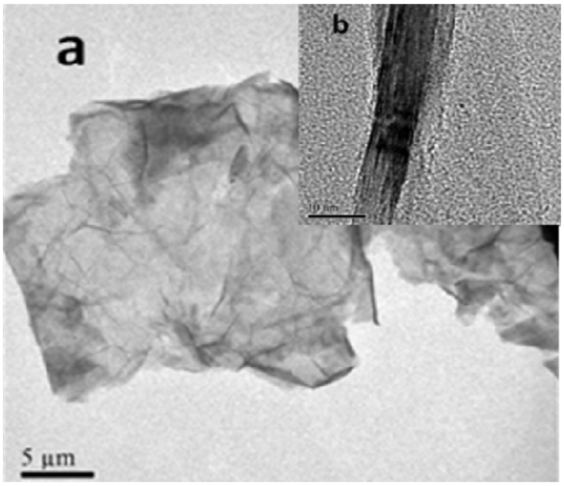

Fig. 2. TEM micrographs of surface (a) and the side edge (b) of the exfoliated GNs.

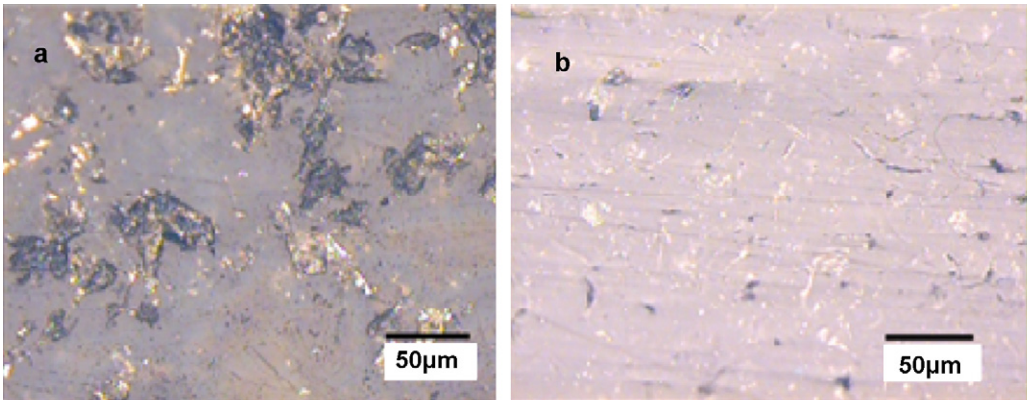

Fig. 3. Surface micrographs of (a) A-plane and (b) B-plane (see Fig. 1) of the 1.2 wt.% GNs-epoxy composite sample.

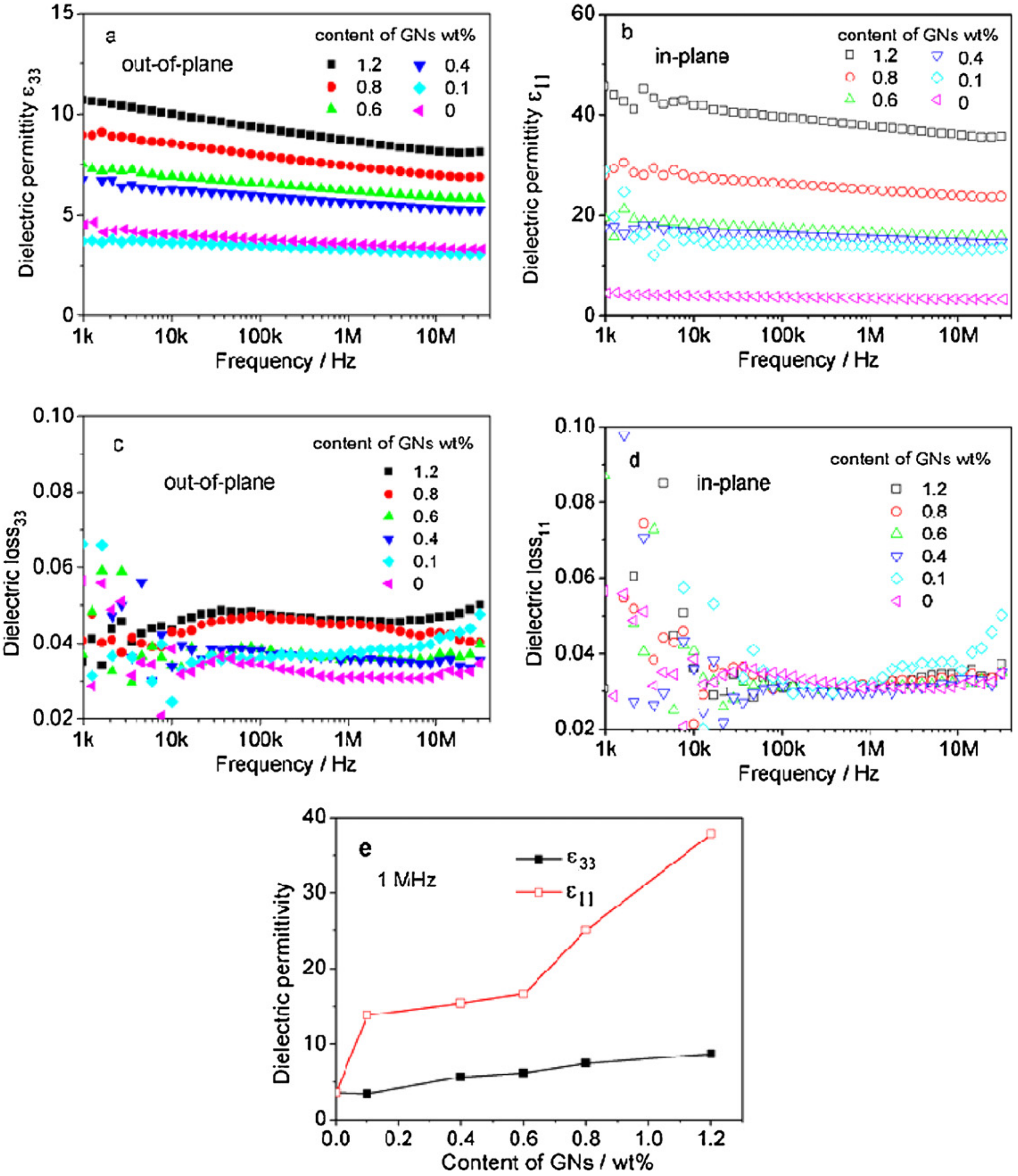

Fig. 4. Dielectric properties of the GNs-epoxy composites: (a) the out-of-plane dielectric permittivity at different frequency, (b) the in-plane dielectric permittivity at different frequency, (c) the out-of-plane dielectric loss at different frequency, (d) the in-plane dielectric loss at different frequency, and (e) comparison between the dielectric constants at 1 MHz.

can be further proved as parallel to the in-plane direction. The self-orientation can be ascribed to the surface tension and the processing method used here. During the solvent evaporation and curing process, the GNs with a large aspect ratio trend to lie down in the resin because of the surface tension. The self-orientation could lead to structural anisotropy of the composites with the planes of the GNs more or less parallel to the sample surface A.

The structural anisotropy of the composites can yield different behaviors along the in-plane and the out-of plane directions. Fig. 4(a) and (b) shows the frequency-dependent dielectric permittivity along these two directions of the composites with different weight percentages of GNs. As seen, the dielectric permittivity of the composites in the two directions presents similar stable frequency dependence, and increases with the increase in the content of the GNs. However, the values of the dielectric constants measured in the two directions are different by a few times. For clear illustration, Fig. 4(e) shows the comparison of the dielectric permittivity in the two directions at 1 MHz. The in-plane dielectric permittivity is about several times of the out-of-plane permittivity. For example, when the content of GNs is 1.2 wt.%, the out-of-plane dielectric permittivity is 8 at 1 MHz, while the in-plane dielectric permittivity is 39. As the GNs are much highly conductive in comparison with the epoxy, the dielectric permittivity of the GNs-epoxy composites in the vicinity of the percolation threshold is described by the power law [11] as:

$$\varepsilon \propto \varepsilon_0 (f_c - f)^{-s} \quad (1)$$

where $\varepsilon_0$ is the dielectric permittivity of the epoxy matrix, $f$ is the volume fraction of the GNs, $f_c$ is the percolation threshold, and $s$ is the critical exponent of about 1. When $f < f_c$, $\varepsilon$ is determined by $\varepsilon_0$ and the distance between the GNs. Obviously, $\varepsilon$ increases with decreasing the distance between the GNs. As the content of the GNs increases, the distance between the GNs decreases. Thus the dielectric permittivity of the composites increases with the increase in the content of the GNs.

The difference between the dielectric constants in the two directions is ascribed to the structural anisotropy of the composites as mentioned above. As the GNs with large aspect ratio self-orientate parallel to the in-plane direction, the distances between the GNs along the in-plane direction are much smaller than those along the out-of-plane direction. Therefore, the dielectric permittivity along the in-plane direction is much higher than that along the out-of-plane direction. The significant difference between the dielectric constants in the two directions reflects the property anisotropy of the composites.

On the other hand, the dielectric loss in both directions is below 0.05, which indicates good insulation as shown in Fig. 4(c) and (d). The epoxy matrix governs the dielectric loss of the composites. The dielectric loss along the in-plane direction fluctuated a lot at low frequency. As the samples are longer along this direction than along the out-of-plane direction, the measurement signal was smaller and influenced much more by errors of instruments at low frequency. The feature of a proper dielectric permittivity and low loss observed in the GNs-epoxy composites makes the composites have potential applications in embedded capacitors.

## 4. Conclusions

Graphite nanoplates-epoxy composites with anisotropy have been prepared via a solution route. Because of the self-orientation of the GNs in the epoxy matrix, the composites present anisotropic dielectric properties. The dielectric permittivity in the direction parallel to the surface of the samples is several times of that perpendicular to their surfaces, and the dielectric loss in both directions is much the same, around 0.04. High dielectric permittivity and low dielectric loss make the composite have potential applications in embedded capacitors.

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