

## EXCEPTIONAL DIELECTRIC PROPERTIES OF SELF-ALIGNED IN-SITU REDUCED GRAPHENE OXIDE/EPOXY NANOCOMPOSITES

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### Abstract

*The electrical conductivities, dielectric properties and electromagnetic shielding efficiency of graphene oxide (GO)/epoxy nanocomposites are studied. Composites containing self-aligned reduced GO (rGO) sheets are fabricated using an all aqueous method. The aligned graphene nanocomposites display significant anisotropy in properties measured in the directions of alignment and perpendicular to it. The rGO/epoxy nanocomposites present a very low percolation threshold of 0.26 wt% as a result of fine dispersion of monolayer rGO sheets and their ultralarge size. The composites exhibit exceptionally high dielectric constants depending on the graphene content due to the charge accumulation at the highly conductive filler/insulating polymer interface according to the polarization principle. The highly dielectric nanocomposites can function as effective electromagnetic interference (EMI) shielding materials.*

### 1. Introduction

As one of the strongest materials, graphene has attracted tremendous attention as a nanoscale reinforcement of a wide range of polymer composites [1,2]. With its exceptionally high carrier mobility and ballistic electron transport properties, graphene is a primary nanofiller in polymer nanocomposites for electrical applications [3]. As a precursor for graphene, graphene oxide (GO) enjoys an abundance of versatile oxygenated groups on its edges and basal planes, allowing high processability and dispersibility in aqueous solutions. These properties make GO an ideal choice for preparation of well-dispersed nanocomposites with an engineered nanostructure and interphase. However, GO suffers from lack of electrical conductivity due to the disruption of its conjugated backbone by the oxygenated groups. Thus, an additional reduction step(s) is often required to restore its electrical conductivity [4].

To fully exploit the potential of graphene as a functional filler, the GO nanosheets need to be rationally assembled within the polymer so that the properties of composites could be tailored for desired effects. The 2D nature of graphene allows assembly of highly anisotropic composites with layered structures, to possess markedly different properties between the directions of alignment and perpendicular to it, which are difficult to be attained using other carbon materials. Reduced GO (rGO) has been used in conjunction with a variety of polymers to prepare conductive polymer nanocomposites. Percolation thresholds ( $P_c$ ) as low as 0.08 and 0.12 vol.% have been achieved in our previous studies on self-aligned rGO/ polyurethane (PU)

[5,6] and rGO/epoxy [7] nanocomposites, respectively. The ultralarge size of GO sheets, their self-assembly into a layered structure and the excellent dispersion of rGO in waterborne polymer matrices were responsible for these remarkably low  $P_c$ . Besides the low  $P_c$  of the nanocomposites and their engineered layered structure, there is a good potential for them to be used in such applications as high dielectric and EMI shielding materials. This paper reports the electrical properties rGO/epoxy nanocomposites with particular emphasis on studying the mechanisms of electrical conduction at different temperatures, dielectric properties and electromagnetic interference (EMI) shielding behavior of the nanocomposites.

## 2. Experimental

GO was produced based on the modified Hummers method [8]. The unsorted GO dispersion was centrifuged at increasingly lower speeds to prepare groups of GO sheets with different sizes [9]. The supernatant was removed after the completion of each round and the precipitate was re-dispersed in water in the following round. The supernatant of the first, second and third rounds were collected as small (S), large (L) and very large (VL) GO sheets, respectively, whereas the precipitate of the third round of centrifugation was collected to label as ultralarge (UL) GO [10]. The process used to prepare epoxy-based composites is as follows [7]. Aqueous GO dispersion at a concentration 1 mg/ml was mixed with epoxy latex and reduced with hydrazine at a GO:hydrazine ratio of 3:1 at 80 °C. Waterborne hardener at a ratio of epoxy:hardener = 5:1 was added to the mixture. The mixture was cured at 60 °C for 24 h to obtain homogenous nanocomposite films. GO/epoxy and rGO/epoxy composites with different graphene contents were prepared. The structure of the nanocomposites was studied using a transmission electron microscope (TEM). The electrical conductivity of cured nanocomposites was measured using a four-point probe in the plane direction and a curve-tracer in the thickness direction. The dielectric properties were measured on an impedance analyzer, and the EMI shielding efficiency was measured using a network analyzer.

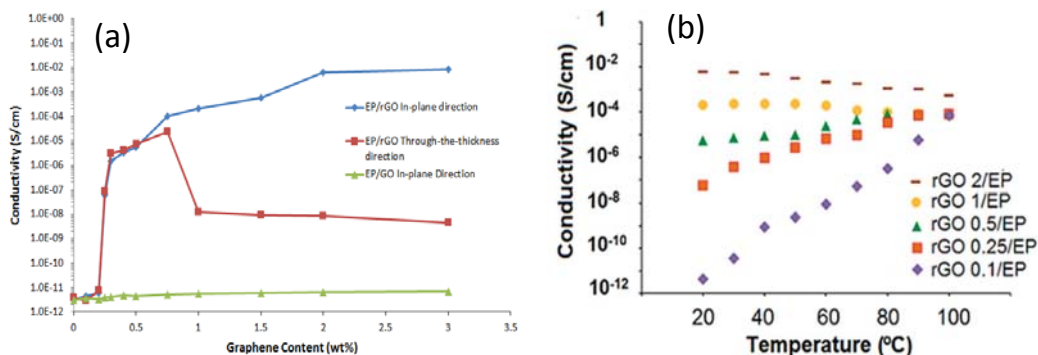


Figure 1. Electrical conductivities of GO/epoxy and rGO/epoxy nanocomposites at different (a) graphene contents and (b) temperatures [7].

## 3. Results and Discussion

### 3.1 Electrical conductivities of GO/epoxy and rGO/epoxy composites

The TEM examination [7] indicates that the graphene sheets were self-aligned into a layered structure when the rGO content was at or above 2.0 wt.%. The self-aligned layered structure resulted in highly anisotropic properties. The directional dependence of the properties was absent in the nanocomposites with low graphene contents which are essentially isotropic in nature. The electrical conductivity of the nanocomposites measured along the two directions

were identical up to about 1 wt.% rGO, confirming the isotropy and random dispersion of graphene sheets at a low content (Figure 1a). However, at graphene contents above this critical value, the trend of conductivity varied differently depending on the direction of measurement: while the conductivity measured in the alignment direction consistently increased, that measured in the perpendicular direction decreased with increasing rGO content. This finding is a reflection of alignment of graphene sheets into a layered structure where there are more electrical contacts between the rGO sheets along the direction of alignment than in the direction perpendicular it. To understand the fundamental mechanism of electrical conduction in nanocomposites, the temperature-dependence of conductivity was measured at different rGO contents (Figure 1b). The conductivity of nanocomposites with low rGO contents, say below 0.5 wt%, was highly dependent on testing temperature and the value increased by a few orders of magnitude when the composites were heated from ambient to 100 °C. However, at high rGO contents, the conductivity varied increasingly in a less temperature-dependent manner, and for the nanocomposites containing 1 wt% rGO or above, the conductivity only marginally decreased with increasing temperature.

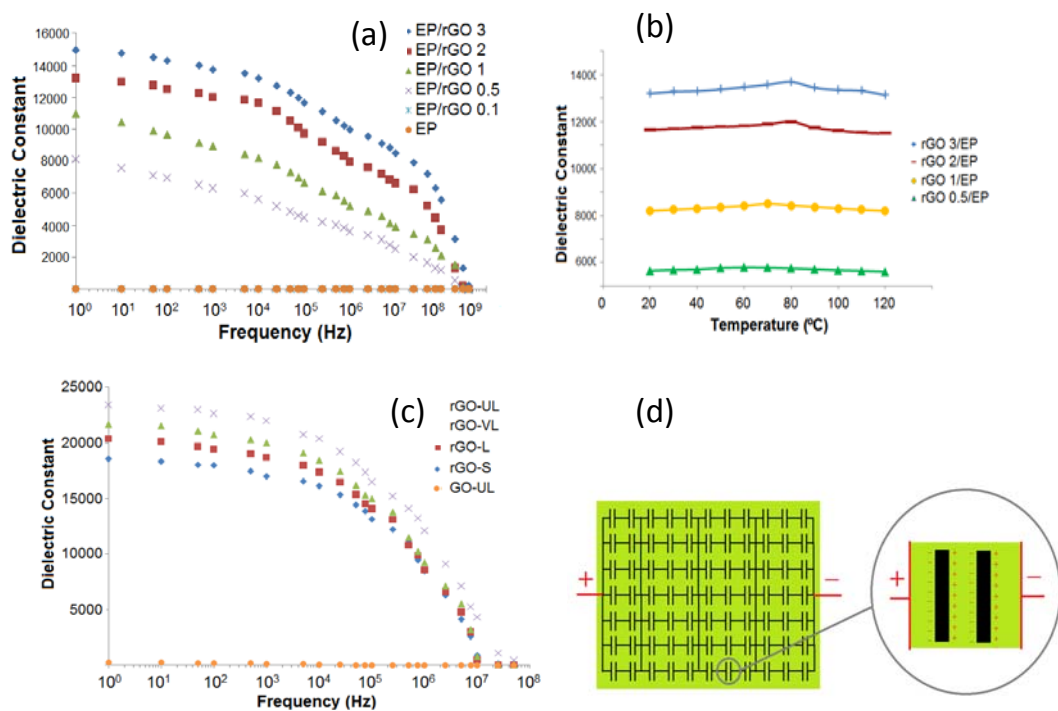


Figure 2. Dielectric constants of rGO/epoxy nanocomposites as a function of (a) frequency and (b) temperature [11]; (c) frequency-dependent dielectric constants of size-sorted GO and rGO papers; (d) schematic of the formation of numerous nanocapacitors in nanocomposites. (S: small; L: large; VL: very large; UL: ultralarge, see [10] for the corresponding rGO sizes)

### 3.2 Dielectric constants of GO/epoxy and rGO/epoxy composites

The dielectric constants of nanocomposites were measured as a function of frequency and temperature (Figure 2a, 2b). Both the neat epoxy and the rGO/epoxy nanocomposites containing 0.1 wt.% graphene presented negligible dielectric constants at all frequencies studied [11]. The very low value of about 5 obtained for the neat epoxy agrees well with the literature [12]. The dielectric properties of conductive polymers follow a percolative pattern. Above the electrical percolation threshold, the conductive networks formed by the nanofillers contribute synergistically to storing the electrical charge at their interfaces with the insulating

polymer, thus producing a highly dielectric nanocomposite. The dielectric constants drastically improved, reaching a value as high as about 15,000 in the composites with 3 wt.% rGO. This value is one of the highest values ever reported for any polymer-based composites. Several structural and material characteristics of the fillers and composites produced are responsible for this result, such as ultralarge size of rGO sheets, excellent dispersion of rGO in epoxy resin, preservation of the stability and dispersion even after reduction in the entirely *in situ* process, and self-alignment of the rGO sheets into a layered structure. The composites held high dielectric permittivities at all temperatures studied. A peak occurred at about 70–80°C, especially in the composites with high rGO contents, which coincides with their glass transition temperature,  $T_g$  [7]. The dielectric constants of polymers also often show a peak in the vicinity of their  $T_g$  as a result of the molecular  $\alpha$ -relaxation. Activation and ordering of electric dipoles are the reasons behind the peak when the molecules start to vibrate vigorously.

Dielectric permittivities of GO and rGO papers were also investigated to compare with those of the nanocomposites (Figure 2c). As expected, the dielectric constants of GO papers (about 70 at 10 kHz) were much lower than the rGO counterparts due to the electrical insulating nature of GO sheets which prohibited the necessary interfacial polarization. Nevertheless, those of rGO papers were even much higher than those of the corresponding polymer nanocomposites. The ultralarge rGO papers delivered remarkable dielectric constants surpassing 24,000 at 1 Hz and ~22,000 at 1 kHz, which to the authors' knowledge are considered the highest values ever reported in open literature. The much higher permittivity in papers than in polymer-based nanocomposites arises from the much higher volume fraction of rGO sheets in papers than in composites. While a maximum of 3 wt% (or equivalent ~1.5 vol%) rGO could be incorporated into epoxy to form a composite because of the unacceptably high viscosities induced by rGO of higher contents, the rGO papers contained 45–50 vol% of rGO [10]. Nevertheless, the rGO papers are unsuitable for dielectric capacitors because of their extremely high dielectric losses varying between 100,000 and 70 at frequencies between 1 Hz and 1 MHz, with a typical value over 3000 at 1 kHz for UL-GO sheets. The very weak or virtually no interfacial bonds between the rGO sheets are to blame .

The good potential of carbon filler/polymer nanocomposites as high-dielectric materials arises mainly from the conductivity mismatch between the fillers and polymer matrix. According to the Maxwell-Wagner-Sillars (MWS) principle, the disparity between the conductivities of two adjacent materials results in polarization and charge accumulation at their interfaces [13]. Therefore, the dielectric properties of nanocomposites are determined chiefly by the nature of the filler/matrix interface, the filler surface area and the inherent conductivity of fillers. More importantly, the orientation of the fillers in a certain direction also plays a very important role in achieving high dielectric constants [14]. Among various mechanisms discussed above, the self-alignment into a layered structure is of particular significance. As the main mechanism of dielectric permittivity in these nanocomposites, the MWS polarization across the rGO/epoxy interface suggests that any pair of adjacent conductive rGO sheets separated by an insulating epoxy thin film can serve as a nanoscale capacitor. Therefore, a typical well-aligned nanocomposite consists of a network of nanocapacitors, as shown in Figure 2d. The huge network containing millions of capacitors can hold an extremely large capacity to store electric charges, enabling the conductive nanocomposite to possess an excellent dielectric permittivity. The anisotropic nature of the aligned rGO/epoxy composites may also present anisotropic dielectric properties between the in-plane and perpendicular directions.

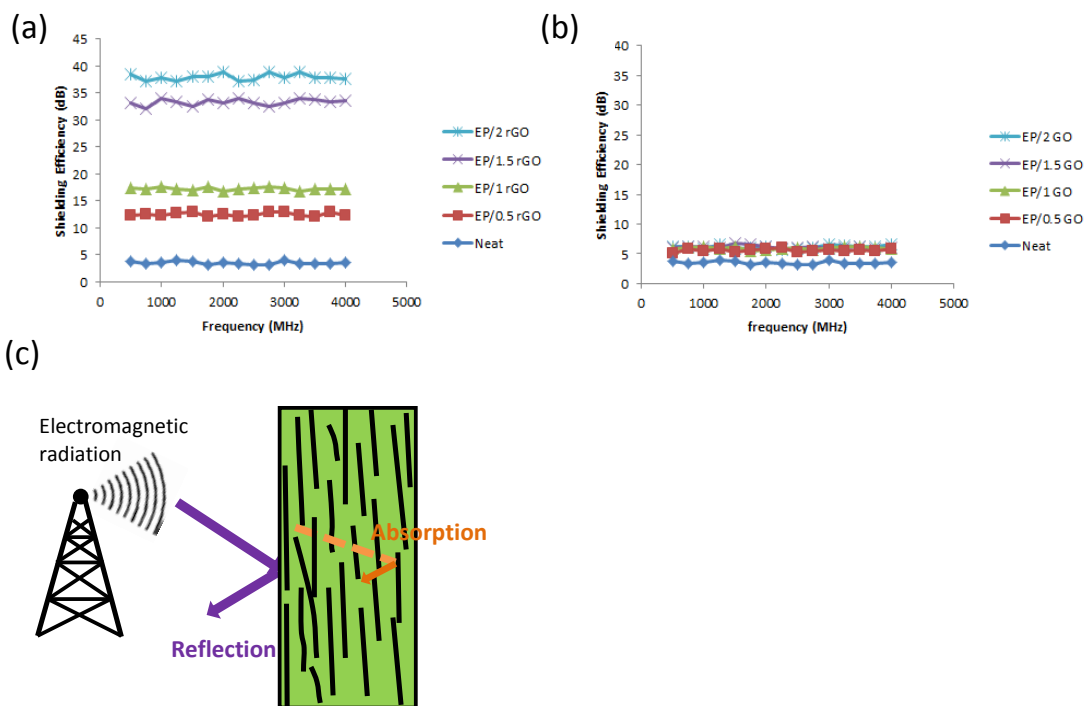


Figure 3. EMI shielding efficiencies of (a) rGO/epoxy and (b) GO/epoxy composites; and (c) schematic of electromagnetic wave shielding through the thickness of composites [15]

### 3.3. EMI shielding efficiencies of rGO/epoxy nanocomposites [15]

One of the most relevant applications of high-dielectric materials is to shield unwanted electromagnetic waves. EMI shielding is particularly important for electronic products where electronic components should be protected from interference coming from other devices/components, while at the same time they should not emit unwanted electromagnetic waves. The heavy weight of metallic EMI shields is undesirable, especially for mobile devices such as smart phones and laptop computers, therefore lighter alternatives have been sought, particularly among polymer-based composites. Carbon-based fillers that hold high electrical conductivities, excellent mechanical properties and low densities, such as carbon fibers, carbon nanotubes (CNTs), CNT papers, graphite and graphene oxide, have been employed to fabricate composites for EMI shielding applications. The EMI shielding efficiency (SE) of polymer-based composites depends on many factors, including the intrinsic electrical conductivity, dielectric constant, magnetic permeability, and content, aspect ratio and dispersion state of conductive fillers. Very few studies have so far been made of the effect of filler alignment on EMI shielding.

With high conductivities and extremely high dielectric constants, aligned rGO/epoxy nanocomposites are an ideal material for EMI shielding to block undesired electromagnetic noises in electronic devices. Indeed, adding rGO sheets boosted tremendously the EMI SE of epoxy. The aligned rGO/epoxy composites delivered exceptional EMI SEs as high as about 38 dB with 2 wt% rGO (Figure 3a), which is considered among the highest for all carbon filler/polymer composites reported in open media. They increased with increasing rGO content, and for a given rGO content they all showed little fluctuation over the entire frequency range studied. The above finding is associated with two unique features of the composites studied here: namely, the rGO sheets aligned in the plane direction contributed positively to shielding the electromagnetic waves that emanate through the thickness direction

(Figure 3c); and the highly conductive rGO/epoxy composites had high charge storage capacities, capable of absorbing the incidental EM waves by polarization in the electric field. In contrast, the EMI SEs of GO/epoxy nanocomposites were found very low, at about 6–7 dB, regardless of GO content, and only marginally higher than about 3 dB of the neat epoxy (Figure 3b). The insulating nature of GO sheets resulted in non-conductive nanocomposites (Figure 1a) with little potential for EMI shielding.

#### 4. Conclusion

The self-aligned RGO/epoxy nanocomposites with highly anisotropic electrical properties are proven to possess exceptionally high dielectric constants and excellent EMI SEs. The large rGO sheets and their alignment into a layered structure play an important role in achieving a dielectric constant well over 14,000 with 3 wt% of rGO at 1 kHz, which is known to be among the highest reported in open literature. The almost parallel rGO sheets along with the interleaved epoxy thin film constitute a network consisting of numerous nanocapacitors which offer a high charge storage capacity to the nanocomposites. The high-dielectric nanocomposites can serve as effective EMI shielding materials due to their high charge absorbing characteristics with a remarkable EMI SE of 38 dB. The comparison of EMI SEs between various materials highlights the advantages of the highly aligned rGO/epoxy composites which can satisfy other requirements of high-performance EMI shielding materials, such as light weight and excellent mechanical properties.

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