Nonlinear DC Conduction Behavior in Graphene Nanoplatelets/Epoxy Resin Composites

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Abstract. Graphene nanoplatelets (GNPs)/Epoxy resin (ER) with a low percolation threshold were fabricated. Then the nonlinear DC conduction behavior of GNPs/ER composites was investigated, which indicates that dispersion, exfoliation level and conductivity of GNPs in specimens are closely related to the conduction of composites. Moreover, it could be seen that the modified graphene nanoplatelets made in this paper could be successfully used for increasing the electric conductivity of the epoxy resin, and the GNPs/ER composites with nonlinear conduction behavior have a good application prospects in the field of intelligent electromagnetic protection.

1. Introduction
Nonlinear DC conduction behavior in inhomogeneous composites which consist of dispersed conducting fillers and insulating matrices has captivated more and more attention in the past decades [1]. A typical feature in such disordered media is the remarkable increase of conductance in the vicinity of the percolation threshold where a spanning conducting network appears of the first time and many physical quantities (i.e., electrical conductance) become critical [2].

Recently, due to the combination of high specific surface areas, peculiar in these single layers of graphite and strong filler–matrix adhesion, graphene has become greatly interesting in polymer science thanks to its possibility of improving the performance of the polymer in which it is embedded [3-5]. Graphene is a single layer of sp2-bonded carbon atoms that can be imagined as an individual atomic plane extracted from graphite. Recent studies have demonstrated that few stacked graphene layers, which basically correspond to partially exfoliated graphite, can be used successfully as a filler for polymers [6]. This filler is commonly referred to as graphene nanoplatelets (GNPs).

As an example, Liang et al. [7] studied the electromagnetic interference (EMI) shielding of graphene/epoxy composites, showing that these systems have a low electrical percolation threshold and good shielding efficiency, indicating that they may be used as lightweight effective EMI shielding materials.

In this research, with the raw material of commercial graphene oxide (GO), several procedures are used to produce modified graphene nanoplatelets with an excellent balance between conductivity and dispersity in matrix (ER), which insures the good characteristic of nonlinear conduction of the specimens.
2. Experimental Procedures

2.1. Materials and Instruments
As the raw material, single-layer graphene oxide (Tanfeng Tech Company, China) is the resource of well exfoliated GNPs. Insulating epoxy resin (E-51), as the matrix, is supplied by Chuzhou Hui-Sheng Electronic Material Company (China). 2-Ethyl-4-methylimidazole (analytical reagent, purity: 99%) is used as hardener obtained from XiYa Reagent Company (China). Hydrazine hydrate (analytical reagent, mass fraction: 85%, Sinopharm Chemical Reagent Company, China) and KH-560 (Nanjing Chuang-Shi Chemical Company, China) are used as reductive agent and coupling agent to modify the single-layer GO.

GNPs and GNPs/ER composites were studied by SEM in order to have a morphological characterization of the specimens. The DC electrical measurements of GNPs/ER composites were performed using a suit of static testing system designed by our research group.

2.2. Preparation of GNPs/ER Composites
In order to obtain GNPs, 600mg GO and 800ml deionized water was mixed in an ultrasonic cleaner for 2 hours. Then, 882.35ml Hydrazine hydrate was poured into the yellow solution while keeping the pH=10. After an eight-hour stirring in magnetic stirring apparatus at 90°C, the suspension was leached for three times and the filter cake was dried in the vacuum freeze drier for 24 hours to obtain the reduced graphene oxide (RGO).

Mixing the deionized water and alcohol with the volume ratio of 1 to 3, 300mg RGO and 3g KH-560 were mixed and dispersed in an ultrasonic cleaner for 2 hours. After a six-hour stirring in magnetic stirring apparatus at 80°C, the suspension was leached for three times and the filter cake was dried in the vacuum freeze drier for 24 hours to obtain the modified graphene (KRGO).

In order to reduce the viscosity of the mixture, 300mg KRGO, 10.02g ER and 50ml acetone were mixed together and dispersed in an ultrasonic cleaner for an hour. Then the mixture was stirred at 80°C for five hours until the acetone evaporated. Finally, as the curing agent, 1.00g 2-Ethyl-4-methylimidazole was added into the mixer, and after ten-minute stirring and ten-minute vacuumizing, the reactive system was poured into disposable dish and allowed to cure for 24 hours at 20°C and for 4 hours at 100°C.

2.3. Characterization and Measurements
A morphological characterization was also performed on the cured samples by using a high resolution scanning electron microscope (SEM). The SEM measurements were performed on a GeminiSEM 300 instrument (ZEISS Company, Germany), with an operating voltage of 3kV. Fig. 1 shows the SEM micrographs of the GNPs after the dispersion in the solvents. To take these micrographs, a droplet of the GNPs suspension was poured in the specific support and allowed to evaporate.

Fig. 2 shows the fracture surface of the cured GNPs/ER composite at 2.65wt%, which could indicate the dispersion of GNPs in the specimen and the surface between filler and matrix.

DC electrical measurements were performed using a suit of static testing system consisting of a high frequency DC regulated power supply, a high-voltage pulse capacitor, an airtight glass box and pneumatic-trigger switches, which is designed by our search group. To ensure good contact, conductive paint was applied on the two circular surfaces of the specimens held between two circular brass electrodes slightly larger in diameter than those of specimens.
Figure 1. SEM micrograph of the suspension of RGO.

Figure 2. SEM micrograph of the suspension of RGO.

Figure 3. The characteristic curve of electric field-conductivity of the cured composites at 2.65wt%.
3. Results and Discussion

3.1. Morphological Investigation of GNPs/ER Composites
According to Fig. 1, it is most likely that the majority of the RGO flakes were constituted by just a few layers, although the SEM did not allow us to exactly affirm how many graphene layers were stacked up in the flakes. Especially, continuous sonication and stirring could improve the exfoliation degree of flakes and reduce the surface area, so the processing condition were considered to be a good compromise between these two aspects. On the other hand, there are some morphological agglomeration and defective on the RGO, which result in the reduction reaction before.

Fig. 2 summarizes the morphological investigation performed on the fractured surfaces of the cured materials. According to the SEM micrographs, it indicates that the modified GNPs could well exfoliate and disperse in epoxy resin, which makes great contribution to the nonlinear conduction of the specimens. Comparing with the morphological results of the suspensions with the SEM on the RGO, there is a partial re-agglomeration occurring during curing procedure, which results in the curing reaction of the composites.

3.2. Nonlinear Conduction in GNPs/ER Composites
The typical characteristics of the nonlinear conduction are that the conductance of a given specimen is no longer a constant. Fig. 3 shows the curve of electric field-conductivity of the cured GNPs/ER composites. The curve, on enough weak voltages, is linear, but with the increase of electric field, it gradually deviates from linearity and bend towards the conductivity axis with increase in bias.

Nonlinear DC conduction behavior above could be affected by many factors, such as a polymer matrix, interfacial interaction between polymer and conducting fillers and compounding process. In summary, the GNPs filler content at 2.65wt% of the composite is close to the percolation threshold, which results that electric field and conductivity fulfill the linear relationship on small electrical fields, and satisfy nonlinear relationship on high fields.

3.3. Conduction Mechanism
Nonlinear conduction behavior in GNPs/ER composites may derive from new conduction channels as a consequence of the applied bias. It is assumed that an insulating bond is equal to an original linear bond. With the GNPs content close to the percolation threshold, the insulating bonds become conducting when the electric field above a critical value goes across them.

The gaps between particles are too large to permit electronic tunneling to take place. As the GNPs content close to the percolation threshold, enough particles begin coming into contact with one another, leading to a specific phase transition from a fully insulated state to flocculated one. Then, the tunneling gaps decrease significantly and the conducting network highly develops.

Meanwhile, insulating ER films inevitably exist inside the clusters because of the physical interaction between particle and matrix. When the gaps between the clusters are small, intercluster and intracluster tunneling or hopping, under sufficiently high electric field, across insulating gaps could bring new conducting pathways, giving rise to supplementary nonlinearity.

4. Conclusions
In summary, GNPs/ER composites with nonlinear conduction behavior and low percolation threshold were fabricated. With the raw material of GO, hydrazine hydrate and KH-560 were used to obtain the modified graphene. According to the SEM micrographs and DC electrical measurements, dispersion, exfoliation level and conductivity of GNPs in specimens are closely related to the conduction of composites.

The nonlinear conduction behavior of GNPs/ER composites has been studied. With the GNPs content close to the percolation threshold, the initial insulating bonds become conducting when the electric field above a critical value goes across them. Therefore, it is shown that the modified graphene nanoplatelets made in this paper could be successfully used for increasing the electric conductivity of the epoxy resin, and the GNPs/ER composites with nonlinear conduction behavior have a good application prospects in the field of intelligent electromagnetic protection.
5. References

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