



Covalent polymer functionalization of graphene for improved dielectric properties and thermal stability of epoxy composites

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ABSTRACT

Incorporation of conductive fillers into polymeric matrix to fabricate the composites with light-weight and excellent dielectric performance has been considered as one of the most promising processes. However, the inevitable high dielectric loss of the composites is still an obstacle for their practical applications, which has become a challenge for a long time, and the solution for this issue is still an open question. In this study, diglycidyl ether of bisphenol-A (DGEBA) molecules were used and grafted onto reduced graphene oxide (RGO) to synthesize DGEBA functionalized RGO (DGEBA-RGO). Various characterizations including TEM, FTIR, UV–visual spectrum, TGA, Raman spectrum and XRD revealed that the DGEBA molecules were grafted onto RGO sheets successfully. The DGEBA-RGO sheets were found to significantly improve the dielectric properties and thermal stability of epoxy compared to the corresponding graphene oxide (GO) and untreated RGO sheets. For instance, at 1 kHz, epoxy composites filled with 1.00 wt% DGEBA-RGO sheets showed a dielectric constant of ~32 at room temperature, which is over 9 times higher than that of neat epoxy (~3.5); meanwhile, the dielectric loss of the composites was suppressed and only 0.08. The enhanced dielectric properties can be well interpreted by the duplex interfacial polarization and the micro-capacitor model. The above outstanding properties should be ascribed to the well dispersion of DGEBA-RGO and the strong interaction between the filler and polymer matrix, which are induced by effective package of grafted DGEBA molecules on the graphene surface.

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1. Introduction

Due to the inherent advantages of being easy to process, flexibility and light weight, polymer-based dielectrics have drawn considerable attention during the past decades [1]. They have been found significant and various potential applications in advanced electronics and electric power systems such as embedded capacitors, actuators, piezoelectric and high energy density pulsed-power devices [2]. These devices usually require high dielectric constant (high- ϵ_r) and low dielectric loss. However, the dielectric constant is generally less than 10 for most of the polymeric materials, so that limits them in applications [3].

Incorporation of the ferroelectric ceramics with high dielectric constant such as barium titanate [4] and calcium copper titanate

[5], or conductive fillers such as metal particles and carbon fillers [6], can significantly enhance the dielectric constant of the resultant composites. For polymer filled with giant dielectric ceramics, there is a good compromise of the polymer host and the ceramic fillers and the dielectric constant can be increased by more than 10–20 times [7]. However, a particulate loading up to 50 wt% or higher is needed to acquire an apparent increase of dielectric constant, which will make the processing difficult and destroy the flexibility. Moreover, at such high loading, the mechanical properties and breakdown strength are deteriorated due to the aggregation of fillers [8]. For the polymer filled with the conductive filler, according to the threshold theory [9], the ultra-high dielectric constant will be achieved near the percolation threshold. Unfortunately, this improvement of the dielectric constant runs the risk of the high dielectric loss [6,10].

Graphene, a one-atom-thick planar sheet of sp^2 -bonded carbon atoms, which has been paid much attention in both academic and

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industry because of its exceptional mechanical, thermal and electrical properties [11]. Due to the high aspect ratio and layered structure, graphene sheets are widely used as ideal filler to prepare the high- ϵ_r polymer composites [12–14], although they are very easy to aggregate on account of the Vander Waals force and π – π stacking, which lead to poor dispersion especially when they are applied in polymer composites. Consequently, the amount of so-called ‘micro-capacitors’ will be largely decreased [15]. More seriously, the aggregation of graphene sheets will induce them contact each other and thus form conductive network, which in turn leads to the leakage current. As a result, the dielectric loss should be absurdly increased, which will limit the application of the resultant polymer based composites as dielectric materials.

To resolve these problems, considerable work has been made, including constructing core–shell structure [7,16], designing multilayered with conductor and insulator [17,18], doping heteroatoms on graphene sheets to improve the polarization [19,20] as well as aligning the sheets to form numerous ‘micro-capacitors’ [6]. Among these methods, one of the most effective ways is the surface functionalization [10,21], which plays a key role to control the dispersion of graphene sheets in polymer host as well as the interface between them. The grafted barrier layers on the surface of conductive filler, which not only enhance the exfoliation/dispersion of sheets and their compatibility in the polymer matrix but also hinder the graphene to contact directly, thus enhancing the dielectric properties of the composites. Fang et al. prepared the NH_2 -functionalized and carboxyl functionalized graphene oxide/polyimide (PI) composite films by *in situ* polymerization, the dielectric constant of this film was 36.9 (@ 1 kHz) at the loading of 4 wt% [14]. He et al. used the 1, 3 dipolar cycloaddition reaction of azomethine ylides to chemically functionalized exfoliated graphite nanoplates (xGNPs) and filled in syndiotactic polystyrene (sPS) matrix to form f-xGNPs/sPS composites with high dielectric constant (~36 at 10wt% @ 1 kHz) [22]. However, the enhanced dielectric constant accompanied by the increased dielectric loss still does not meet the critical requirements of energy storage applications, where both high dielectric constant and low dielectric loss are required. Considering the fact that polymer macromolecule chains possess excellent insulating properties, it is promising to fabricate RGO/epoxy composites with excellent dielectric property through grafting epoxy polymer onto RGO surface.

Herein, we developed a facile and effective method to graft diglycidyl ether of bisphenol-A (DGEBA) molecules onto GO surface and subsequently reduced by hydrazine hydrate to synthesize DGEBA functionalized RGO (DGEBA-RGO). Epoxy resin was selected as the matrix since it has a wide range of applications such as adhesive, coatings, electronic encapsulants and insulating layers, as well as the polymer matrix for the dielectric layer of embedded capacitors. The epoxy composites with different loadings of DGEBA-RGO, GO and RGO sheets were prepared and comparatively investigated. The related mechanism for the improved dielectric properties was also studied.

2. Experimental

2.1. Materials

Natural graphite was provided by Huadong Graphite Factory (Pingdu, China). The oxidative and reductive agents including concentrated sulfuric acid, concentrated nitric acid, hydrochloric acid, potassium chlorate and hydrazine hydrate (80%) were supplied from Beijing Chemical Factory without further purification. Diglycidyl ether of bisphenol-A (DGEBA, Wuxi Resin Factory of Bluestar New Chemical Materials Co., Ltd.) was served as matrix as well as the modifying agent in this work, the chemical structure of

DGEBA molecule is shown in Fig. 1. The mixtures (100:1 by weight) of 4-methylhexahydrophthalic anhydride (MHHPA, Puyang Hui-cheng Chemicals Co., Ltd.) and the N, N-Benzylidimethylamide (Sinopharm Chemical Reagent Co., Ltd.) were used as curing agent in this study.

2.2. Preparation of DGEBA-RGO

The GO sheets were prepared using the modified Hummer's method [23]. The details for preparation of DGEBA molecules functionalized GO (DGEBA-GO) can be found in our previous work [24]. For the preparation of DGEBA-RGO, typically, 100 mg DGEBA-GO was dispersed in 200 ml H_2O to form a homogenous suspension after sonication for 30 min, then 10 ml hydrazine hydrate (80%) was added into the above suspension, the mixture was subjected into the oil bath, stirred and refluxed under 80 °C for 4 h; after that, the suspension was filtrated with Teflon filter (0.45 μm) and washed by H_2O for 5–6 times; at last, it was dried in vacuum at 80 °C for 12 h. For comparative study, the RGO was produced by using the same process without surface modification.

2.3. Fabrication of DGEBA-RGO/epoxy composites

The epoxy composites filled with GO, RGO and DGEBA-RGO were fabricated by the following procedure: weighted amount of sheets and epoxy resin were first dispersed in acetone by sonication for 30 min. To improve the dispersion of the graphene sheets effectively, the ball milling was employed to break up the agglomerates of the sheets. It should be noted that, to avoid the high energy destroyed the structure of graphene sheet, the rotated speed and ball milling time should be controlled at 250 rpm and 4 h [25,26], respectively. Then the solution was put in a vacuum at 80 °C for 24 h to remove the solvent. After that, the curing agent was added to mixture by mechanical stirring (curing agent to resin by weight ratio of 170:185). After degassing process at 60 °C for 30 min, the pre-polymer was poured into the pre-heated steel molds, through the curing process (30 min at 90 °C, and 60 min at 120 °C, afterwards 30 min at 140 °C, finally 120 min at 160 °C.), the samples with diameter (12.5 mm) and thickness (1.0 mm) were obtained by polishing process, as shown in Fig. 1. The neat epoxy was fabricated by the same procedure as described above without filler.

2.4. Characterization

The morphologies and microstructures of GO, RGO and DGEBA-RGO were observed by a transmission electron microscopy (TEM, HITACHI H-7650). The sheets were first dispersed in acetone by sonication for about 10 min, then using a carbon coated 200-mesh copper grids to collect them for TEM observation. FT-IR scans (Nicolet 7000, Antaris) were done for assessment of the covalent grafting of DGEBA molecules on to GO sheets. Raman spectra were performed on a SENTERRA Micro Raman Spectroscopy, samples were deposited on the wafer directly without solvent and a laser excitation of 633 nm was used. To detect the reduction of GO and the interaction between the DGEBA molecules and graphene sheets, the ultraviolet–visible (UV–vis) spectra were recorded by an UV–VIS–NIR spectrophotometer (UV-3600, SHIMADZU), scanned area was from 200 to 600 nm, acetone was used as the reference solution. X-ray diffraction (XRD) measurements were carried out at a scan rate of 2 min^{-1} using a D/Max2550V X-ray diffractor (Rigaku, Japan) at room temperature. Thermogravimetric analysis (TGA) of the fillers as well as its polymer composites was performed by TA instruments Q600 under the N_2 atmospheres with heating rate of 10 °C/min and 20 °C/min, respectively. The dispersion state

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