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Fabrication and characterization of structural/dielectric three-phase composite: Continuous basalt fiber reinforced epoxy resin modified with graphene nanoplates

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ABSTRACT

A kind of multifunctional composite with combined dielectric and mechanical properties was prepared using conductive nanofiller to modify continuous fiber-reinforced polymer composite. The three-phase graphene nanoplates/basalt fiber/E-51 epoxy resin (GNPs/BF/E-51) composite was designed as structural/dielectric composite that could perform energy storage process and sustain mechanical loading simultaneously, possessing potential application as dielectric layer in structural capacitors. The effects of GNPs content on morphology, mechanical, dielectric and electrical properties of E-51 epoxy resin and BF/E-51 composite were investigated. Dielectric mechanism was proposed based on interfacial polarization and electron conduction process. Experimental results show that dielectric permittivity, dielectric loss and alternating-current conductivity sharply increase when GNPs loading reaches 1 wt% for GNPs/E-51 and 0.24 wt% for GNPs/BF/E-51, owing to different dispersing state of GNPs in composites. Mechanical properties of GNPs/BF/E-51 composite increase after the addition of GNPs. GNPs/BF/E-51 composite with suitable GNPs content demonstrates outstanding integrative dielectric and mechanical properties.

1. Introduction

Driven by severe environmental disruption, forecasted shortage of fossil energy and the development of modern technology, the demand of green and efficient electrical energy storage devices increases gradually. Structural/dielectric composite is a kind of multifunctional material with the abilities of storing electrical energy based on dielectric polarization of capacitor and sustaining mechanical loading simultaneously. It is believed to be a key material to achieve the target of fabricating greener, safer, easier to transport, more lightweight and space saving energy storage devices, which can be utilized in many applications, such as hybrid electric vehicles [1] and pulsed power systems [2,3].

Several strategies have been developed to fabricate structural/dielectric composites with dielectric and mechanical bulk materials. One method is to decorate high-strength fiber core with a ferroelectric ceramic shell, where the fiber acts as the load-bearing material as well as an inner electrode and the ferroelectric ceramic shell plays the role of dielectric layer. Based on this method, the multifunctional fibers of SiC fiber@$BaTiO_3$ and carbon fiber@barium strontium titanate (BST) were fabricated through high temperature sintering process and two-step hydrothermal reaction, respectively [4,5]. Though relatively high dielectric permittivity can be achieved, however, the preparation of these composites usually requires time-consuming and complicated chemical synthesis, and a further integration process is needed for preparing macroscopic specimens.

Another alternative approach is to use electrically insulating fiber reinforced polymer composite as the dielectric layer. O'Brien et al. [6,7] fabricated structural capacitors by inserting a dielectric layer of glass fiber/epoxy prepreg between two layers of metalized polymer film electrodes. The dielectric permittivity ranging from 4.63 to 6.08 and tensile strength ranging from 170 MPa to 560 MPa were achieved. In a follow-up study, structural capacitors with the energy density exceeding 0.90 J/cm^3 were prepared by improving processing conditions and electrode selection [8]. In some cases, dielectric filler or conductive filler was added in composite to improve dielectric and mechanical properties. Fiber glass/polymethyl methacrylate (FG/PMMA) structural dielectrics containing neat or Poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT-PSS) coated $BaTiO_3$ particles were studied by

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Stefanescu et al. [9]. The results showed that the dielectric permittivity of the composites modified with $BaTiO_3$ and $BaTiO_3$@PEDOT-PSS nanoparticles were about 13 and 16 (@ 1 kHz), and the tensile strengths were 208 MPa and 223 MPa, respectively. The core-shell structure of carbon nanotubes/silicon oxide (CNT@SiO_2) reinforced glass fiber composite was fabricated with the dielectric permittivity of 7.64 (@ 1 MHz) and tensile strength of 248 MPa at the filler loading of 4 wt% [10]. These fiber reinforced polymer composites can be fabricated using traditional composite processing methods. The difficulty is how to obtain high dielectric permittivity with low dielectric loss. In addition, mechanical property should be further enhanced if the composite is used in high load-bearing environment.

It is well documented that continuous fiber reinforced thermosetting composite materials possess outstanding mechanical performance [11–13]. Continuous basalt fiber (BF) and its epoxy matrix composites are highly favored in transportation, construction and petrochemical industries and the field of national defense due to inherent good performances, such as mechanical property, chemical stability, heat, corrosion and abrasion resistance, environmentally friendly and low-cost features. Especially, BF possesses better dielectric and mechanical properties than glass fiber, and the advantages of outstanding hygroscopicity and chemical stability ensure the stability and service life in actual application. Based on the above reasons, we believe that BF is a promising material in structural/dielectric composite. In addition, conductive nanofillers are capable of increasing dielectric property of composite at a very low filler loading [14–16]. It is possible to achieve good dielectric and mechanical properties simultaneously by modifying fiber reinforced composites with conductive nanofillers. Many works have been carried out to improve mechanical properties of fiber reinforced polymer composites using conductive nanofillers [17–19], but there are few works concerning on dielectric property. Among various conductive nanofillers, graphene, a two-dimensional planar sheet with large aspect ratio and specific surface area, is well accepted to be capable of enhancing dielectric property of polymer at low filler loading [14,20,21]. Based on the discussion above, it is anticipated that by introducing graphene nanoplates (GNPs) into BF reinforced polymer composite, a three-phase structural/dielectric composite with the combined advantages of high dielectric permittivity, low dielectric loss, high mechanical property and ease of processability might be obtained. Dielectric mechanism of this three-phase composite should be studied and understood for optimizing material system and processing conditions.

In this paper, GNPs were used as conductive nanofiller to apply doping modification to E-51 epoxy resin matrix and BF/E-51 composite. The three-phase GNPs/BF/E-51 composite was designed as structural dielectrics for multifunctional capacitors that require stiffness, strength and energy storage capability. GNPs was used to increase dielectric permittivity and epoxy resin ensured good processability of composite and strong interfacial bonding, while BF provided high strength and modulus and moderate dielectric property. Fourier transform-infrared spectrum (FT-IR), transmission electron microscope (TEM) and atomic force microscope (AFM) were used to characterize the structure and morphology of GNPs. Scanning electron microscope (SEM), metallurgical microscope, precision impedance analyzer and universal testing machine were employed to characterize the structure and properties of GNPs/E-51 and GNPs/BF/E-51 composites. By changing the content of GNPs in GNPs/E-51 and GNPs/BF/E-51 composites, the influences of GNPs on morphology, mechanical properties, dielectric and electrical properties were studied. The mechanism of interfacial polarization as well as electron conduction process of the composites were discussed, which were related to the dispersing state of GNPs in composite.

2. Experiment

2.1. Materials

All materials in this study are commercially available. GNPs with the average thickness of 2.5 nm were purchased from Tangshan Jianhua Technology Development Co., Ltd. The GNPs were prepared through the method of low-temperature reduction of graphene oxide, which was prepared from graphite based on the Hummers method. The reduction process was conducted by microwave heating. Basalt fiber unidirectional fabric with areal weight of 300 g/m^2 was purchased from Shanxi Basalt Fiber Technology Co., Ltd. The BF in the fabric has filament diameter of 13 μm, tensile strength of 2800 MPa and tensile modulus of 91 GPa. Bisphenol A epoxy resin, named E-51, was purchased from Nantong Xingchen Synthetic Material Co., Ltd. Curing agent BC126 was purchased from Dasen Material Technology Co., Ltd.

2.2. Fabrication of GNPs/E-51 composite

For the fabrication of GNPs/E-51 composites with different filler loading levels (0.3 wt%, 0.5 wt%, 1 wt%, 1.5 wt% and 2 wt%), GNPs were added into N,N-dimethylformamide (DMF) solvent and then treated by four cycles of ultrasonication using an ultrasonic cell disruption system. Then, E-51 epoxy resin was dissolved in DMF solvent and mixed with the as-prepared GNPs suspension, followed by 1 h of ultrasonication using a bath sonicator. Subsequently, the obtained mixture suspension was heated and stirred to evaporate DMF solvent at about 100 °C for 6–8 h. The curing agent BC126 (the mass ratio of E-51 to BC126 was 100:84) was added and heated for 30 min in a vacuum oven at 50 °C to release DMF solvent and remove bubbles. Finally, the GNPs/E-51/BC126 system was cast into a preheated mold and cured at 120 °C for 2 h.

2.3. Fabrication of GNPs/BF/E-51 composite

The GNPs/BF/E-51 composite was fabricated by means of hand lay-up and hot press molding. The prepared uncured GNPs/E-51/BC126 was coated on basalt fiber fabrics, then the fabrics were unidirectionally laid up layer by layer and cured at 120 °C for 2 h under 0.8 MPa in a hot press machine. The GNPs/BF/E-51 composite laminates with GNPs mass fractions of 0.07 wt%, 0.15 wt%, 0.24 wt%, 0.35 wt% and 0.41 wt% were prepared.

2.4. Characterization

FT-IR spectrometer (Nexus 470, USA) was used to study the functional groups of GNPs. TEM (JEM-2100, Japan) was employed to characterize the microstructure of GNPs. AFM (ICON, USA) was used to measure the thickness of GNPs. SEM (JEOL 7500, Japan) was applied to investigate the fracture morphology of GNPs/E-51 and GNPs/BF/E-51 composites. The processing quality of GNPs/BF/E-51 composite was assessed using metallurgical microscope (LEICA DM4000, Germany) [22]. Dielectric and electrical properties of the composites were measured on a precision impedance analyzer (Agilent 4294A, USA) at the frequency range of 10^2–10^7 Hz under applied voltage of 500 mV at room temperature. Dielectric and electrical tests were performed in accordance with ASTM D150-2011 and ASTM D257-2014, respectively. Mechanical properties were tested in tensile mode and three-point bending mode at a rate of 2 mm/min using an universal testing machine (Instron 5565, USA), in accordance with GB/T 3356-2014 and GB/T 3354-2014, respectively.