Composites Science and Technology 141 (2017) 48–55

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Barium titanate coated and thermally reduced graphene oxide towards high dielectric constant and low loss of polymeric composites

Yan-Jun Wan [a, b], Peng-Li Zhu [b], Shu-Hui Yu [b], Wen-Hu Yang [b], Rong Sun [b, **], Ching-Ping Wong [c], Wei-Hsin Liao [a, *]

[a] Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China
[b] Center for Advanced Materials, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, China
[c] Department of Electronic Engineering, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China

A R T I C L E I N F O

Article history:
Received 19 September 2016
Received in revised form
13 December 2016
Accepted 13 January 2017
Available online 14 January 2017

Keywords:
Polymer-matrix composites (PMCs)
Dielectric properties
Thermal properties
Scanning electron microscopy

A B S T R A C T

Novel barium titanate (BT) layer coated and thermally reduced graphene oxide (TGO) hybrid sheets (BT@TGO) were successfully synthesized by a facile sol-gel method combining with thermal treatment process (600 °C) under nitrogen atmosphere. The BT precursors attached on graphene oxide (GO) sheets were crystallized into perovskite structure with high permittivity and GO sheets were thermally reduced heavily at such high temperature simultaneously. The hybrids were used as filler to fabricate high performance dielectric polyvinylidene fluoride (PVDF) composites by solution blending method and their dielectric performances were studied. It was found that addition of BT@TGO decreases the electrical conductivity when compared with TGO/PVDF composites and pure PVDF, and BT@TGO/PVDF composites exhibit not only high dielectric constant but also low dielectric loss. For instance, at 10^3 Hz, the dielectric constant of PVDF composites containing 8.0 wt% BT@TGO is up to ~56.3 at room temperature, which is over 5 times than that of pure PVDF polymer (~10.3). More importantly, the dielectric loss is suppressed and only 0.058, which should be attributed to the effective encapsulation of insulating BT layer with high permittivity on the TGO surface. In addition, the improved thermal stability and crystallization behavior of BT@TGO/PVDF composites were also investigated.

1. Introduction

With the continuing miniaturization and increase of power density in electronic devices, higher and stricter requirements are desired for advanced electronic packaging materials [1]. High dielectric constant (high-*k*) polymer-based composites exhibit great potential applications in micro-electronics such as embedded capacitor, gate dielectric and electrical energy storage due to their light-weight, good mechanical properties, simple fabrication process and facile processability [2,3]. Generally, most polymers possess low dielectric constant (typically less than 10) due to the negligible contribution of the ionic component to total dielectric constant [4]. A promising way to increase dielectric constant of polymer is using high permittivity nanoparticles, such as barium titanate (BT) [5] and calcium copper titanate [6] as fillers. However, an effective improvement of the dielectric constant is not observed until high concentration of the filler has been added into the polymer matrix, which will induce severe aggregation and deteriorate the mechanical properties. Moreover, as a consequence of the high loading of particles, the density of polymer composites increases and it suffers from decreased electric breakdown strength [7].

Over the past few years, high-*k* polymer composites based on electric conductors, such as metallic particle, graphene and carbon nanotube (CNT) [8] have gained significant attention because of the low filler concentration and great possibility to integrate the performance advantages of polymer [9]. Although, polymer composites based on conductor with super high-*k* have been achieved [10,11], the high dielectric loss caused by the leakage current is still an enormous challenge, which limits their applications. Therefore, the key issue is to prevent direct contact between conductive fillers to improve the dielectric constant and suppress dielectric loss of the polymer-based composites. A lot of efforts

---

* Corresponding author.
** Corresponding author.

E-mail addresses: rong.sun@siat.ac.cn (R. Sun), whliao@cuhk.edu.hk (W.-H. Liao).

http://dx.doi.org/10.1016/j.compscitech.2017.01.010
0266-3538/

have been made to fulfill the above purpose including surface modification of conductors [12,13], construction of multi-layered structure with conductor and insulator [9], deposition of metallic particles on the surface of BT [14,15], and combination of CNT with insulated graphene oxide sheets [16,17]. In our previous work, a kind of polymer chains were employed to modify the graphene sheets by forming covalent bond, which improves the dispersion of graphene and the interface between sheets and epoxy matrix, thus enhanced mechanical properties and dielectric performances were obtained [13,18]. However, when the filler concentration is up to 1.8 wt%, the dielectric loss increases to ~1.0 at 1 k Hz [13].

Most of the previous work focused on surface functionalization and chemical reduction of GO [19], which involves introduction of toxic reduction agents such as hydrazine hydrate. Another effective and eco-friendly method to reduce GO sheets is thermal treatment process, which usually needs 600 °C or a higher temperature to complete the optimal reduction [20]. Unfortunately, graphene sheets modified by organics (polymer chains or small molecules) are unable to withstand such high temperature [12,21].

Nevertheless, the way of thermally reduced process provides a facile route for decoration of oxides on graphene sheet. To further improve the dielectric performance of graphene polymer composites, i.e., high-*k* and low dielectric loss, in this study, we provide a simple sol-gel strategy integrating with thermal treatment process (600 °C) to synthesize thermally reduced graphene oxide (TGO) hybrids covered with insulating and high permittivity BT layer (BT@TGO), in which each graphene sheet was decorated with BT layer uniformly and continuously. The thermal treatment process, on one hand, reduces the insulating GO to conductive TGO. On the other hand, it makes the amorphous precursor of BT crystallize into perovskite structure with high-*k* under the high temperature. Thus, an insulator-conductor-insulator sandwiched 2D nanostructure can be constructed, which is crucial to improve the dielectric constant and suppress the loss of its polymer composites simultaneously. Polyvinylidene fluoride (PVDF) was selected as matrix since it is one of the most extensively studied and attractive polymer-based matrix owing to its fascinating virtues, such as relatively high dielectric constant and thermal properties. The BT@TGO/PVDF composites were fabricated by solution-blending and hot press method. The dielectric and thermal properties of resultant composites were investigated.

2. Experimental

2.1. Materials

Natural graphite powder was supplied by Yifan Graphite Factory (Shanghai, China). Barium acetate, tetrabutyl titanate, acetic acide, acetylacetone, polyethylene glycol with molecular weight of 200 (PEG-200) and the oxidation agent including potassium chlorate, nitric acid and sulfuric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification.

2.2. Synthesis of BT@TGO

Graphene oxide (GO) was synthesized from Hummer's method with some modifications [22]. To synthesize BT@TGO, GO sheet with BT precursor was prepared by sol-gel method firstly and the Ba and Ti cations were controlled strictly at 1:1 by molar ratio. Typically, 0.04 g GO was dispersed into acetylacetone (50 ml) by sonication for 30 min to form a homogenous solution with the assistance of PEG-200 (1.489 g), then 1.701 g (5 mmol) tetrabutyl titanate was dissolved into the above mixed solution by stirring for 5 min. Meanwhile, 1.277 g Barium acetate (5 mmol) was dissolved into acetic acid (5 mL) with vigorous stirring for ~30 min at 60 °C. The above solution was added dropwise into GO solution with stirring for ~30 min then aged at room temperature for 24 h. After that, the resulting suspension was filtered and the obtained paste was dried at 60 °C then calcined in a tube furnace under N_2 atmosphere with the following procedure: 2 h at 200 °C, afterwards 2 h at 400 °C and finally 2 h at 600 °C. The scheme of the procedures for BT@TGO was shown in Fig. 1a. For the sake of comparison, the as-prepared GO sheets were treated with the some thermal-reduction process without BT.

2.3. Fabrication of BT@TGO/PVDF composites

The BT@TGO/PVDF composites were prepared by solution blending and hot pressing process. Weighted powder of BT@TGO and PVDF matrix were dispersed in ethanol solution by magnetic stirring for 3 h. Then, the suspension was treated by sonication with the frequency and power of 40 kHz and 1 kW, respectively, to further disperse the BT@TGO sheets homogeneously. Afterwards, the suspension was dried at 60 °C for 10 h to get the mixed powder and then molded by hot pressing at 180 °C and 15 MPa for 15 min. At last, a disk shape with 12 mm in diameter and 1 mm in thickness was obtained by polishing process and both sides of the rounded sample were painted with silver paste as electrode. The pure PVDF and PVDF composites filled with TGO were fabricated by the same procedure as described above.

2.4. Characterization

The morphologies and microstructures of fillers and the PVDF composites were observed by a SEM (Nova Nano SEM450, FEI). BT@TGO and BT layer were observed by a transmission electron microscopy (TEM, Tecnai G2 Spirit120kV). For SEM observation of composites, samples were fractured after they were cooled by liquid nitrogen. X-ray diffraction (XRD) measurements were conducted at a scan rate of 2 min^{-1} using a D/Max2550V X-ray diffractor (Rigaku, Japan). To identify the elemental compositions of TGO and BT@TGO, X-ray photoelectron spectroscopy (XPS, VG scientific ESCA Lab 220I-XL) was used. Thermogravimetric analysis (TGA) of fillers and PVDF composites were performed with heating rate of 10 °C/min using TA instruments Q600 under air and N_2 atmospheres, respectively. Differential scanning calorimeter (DSC, TA instrument Q20) was employed to study the crystallization behaviors of PVDF and its composites from 30 to 175 °C. High precision impedance analyzer (Agilent 4249A) was used to measure the frequency dependent capacitance and dielectric loss as well as the alternating current (AC) conductivity in the frequency range of 10^2–10^7 Hz at room temperature. DC breakdown strength was measured by dielectric strength tester (CS9912BX, Allwin Instrument Science and Technology co. Ltd, China). The dielectric constant of the composites in this study was calculated by the following equation:

$$k = d \cdot C / (\varepsilon_0 \cdot S)$$

where d is the thickness of the sample, C is the capacitance (obtained from impedance analyzer), ε_0 is the dielectric constant of vacuum, which equals to 8.85×10^{-12} F/m approximately, and S is the area of the electrode.

3. Results and discussions

3.1. Morphology and characterization of BT@TGO

Fig. 1a presents the synthesis scheme of BT@TGO, in which the