Research Article

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Enhanced dielectric properties and breakdown strength of polymer/carbon nanotube composites by coating an SrTiO₃ layer

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Abstract: In this work, strontium titanate (STO) was coated on the surface of carbon nanotubes (MWCNTs) through a sol–gel method to form a core–shell structure hybrid powder (STO@MWCNTs). This powder was then added to polydimethylsiloxane to prepare a flexible high-K composite. As coating, STO effectively prevents the overlap and agglomeration of MWCNTs, thereby passivating the percolation threshold of the composite. STO increases the dielectric properties of the composite as a high dielectric ceramic. Under a low filler loading amount of 11 wt%, the dielectric constant and dielectric loss of the composite are 53 and 0.1, respectively. In addition, the composite can still maintain superior breakdown strength and mechanical properties, given the relatively low filler concentration. The enhanced dielectric properties, breakdown strength, and tensile strength make the composite suitable for application as dielectric material in flexible and stretchable energy storage equipment.

Keywords: carbon nanotubes, strontium titanate, sol–gel method, composites

1 Introduction

Polydimethylsiloxane (PDMS) has been widely explored in capacitive sensors, electromechanical actuators, and other stretchable electronics due to its excellent flexibility and stable electrical and mechanical properties (1). However, PDMS as a dielectric matrix has a dielectric constant much lower than that of inorganic ceramics, which makes it gradually unable to satisfy the requirements for the miniaturization and integration of new electronic equipment (2). Recently, all-organic polyimide/polysulfone (PI/PSF) composite films have been successfully prepared by *in situ* polymerization (3). When the PSF content is 40 wt %, the PI/PSF-40 has the highest dielectric constant of 6.40 at 1 kHz and excellent mechanical properties. However, the dielectric constants of PI/PSF composites still need to improve more.

The dielectric properties of polymers have been improved by adding a certain concentration of fillers to the polymer. The most common method is adding high dielectric ceramics to the polymer matrix. Such fillers usually contain BaTiO₃ (4,5), TiO₂ (6), SrTiO₃ (7), and CaCu₃Ti₄O₁₂ (8,9). Such composites generally require a high filler volume fraction (>50 vol%) for improved dielectric properties, greatly diminishing the mechanical properties and breakdown strength of the composites. In order to maintain the breakdown strength, bilayer polyetherimide-BaTiO₃/P(VDF-HFP) composites have been rationally designed (10). In addition, when mica is added into polyimide matrix as a filler, the dielectric constant of polyimide/mica hybrid film declined. And the multilayer structured mica would disturb the polarization of the hybrid (11). Another method is adding conductive fillers to improve the dielectric properties of the composite (12–14). However, the dielectric constant of the composite can be significantly increased only when the conductive filler is close to the percolation threshold, which increases the risk of composite breakdown and dielectric loss. In general, the use of a core–shell structure is an effective method that improves

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the dielectric properties of conductive filler/polymer composites. Our previous works have investigated the core-shell structure of carbon nanotubes (MWCNTs), such as polyhedral oligomeric silsesquioxane, boron nitride, ionic liquids, and some polymers (15–21). An insulating shell is usually coated on the surface of the MWCNTs to reduce the surface energy and prevent MWCNTs from being in contact with each other to cause increased dielectric loss.

High dielectric ceramics are used as the shell of MWCNTs to control the contact of conductive fillers in the composite and obtain low dielectric loss and high dielectric constant. In this work, a core-shell-structured hybrid is synthesized by coating a strontium titanate (STO) shell on the MWCNTs via the sol-gel method and compounded with PDMS to prepare percolative polymer composites. STO-coated MWCNTs (STO@MWCNTs) can effectively improve the dielectric constant of PDMS composites and maintain the dielectric loss at a low value. Given the dual function of the STO shell, the dielectric constant of the composite can reach 53 at low loading (11 wt%), and the dielectric loss is only 0.1. In addition, the STO@MWCNTs/PDMS composites can maintain superior breakdown strength and mechanical properties.

2 Experimental

2.1 STO@MWCNT hybrid preparations

STO@MWCNTs were prepared by sol-gel processing in our laboratory (7). In detail, $\text{Sr}(\text{NO}_3)_2$ (0.013 mol, Aladdin) was dispersed in 25 mL deionized water and was labeled “solution A.” Tetrabutyl titanate (0.013 mol, Aladdin) and 2 mL acetyl acetone (Macklin) were dissolved in 40 mL absolute ethanol and was labeled “solution B.” Afterward, A was added to B and stirred for approximately 1 h to form a sol at 40°C. COOH-MWCNTs (0.1 g; carboxyl groups: 1.23 wt%, diameter: 20–40 nm) and 0.1 g sodium dodecyl benzene sulfonate (SDBS, Guangfu) were added to the sol solution and dispersed via sonication for 1 h. The sol solution was then stirred for about 3 h at 40°C. The precipitate was filtered, dried, and sintered at 800°C for 2 h under a nitrogen flow to obtain STO@MWCNTs.

2.2 Preparation of composites

The Dow Corning Sylgard 184, curing agent, and different weight ratios of STO@MWCNTs (0, 3, 5, 7, 9, and 11 wt%) were vigorously stirred under sonication for 1 h to obtain

a thorough dispersion. After the removal of ethyl acetate, the mixture was cast into a mold and cured in a thermal oven at 150°C for 30 min. The resulting product was referred to as STO@MWCNTs/PDMS composites. MWCNTs/PDMS composites were also prepared using the method described above.

2.3 Characterization

The morphology of the STO@MWCNTs and the fracture plane of composites were determined through field-emission scanning electron microscopy (SEM; HITACHI S-4700). The Agilent 4294A with 16451B fixture (from 40 Hz to 30 MHz) was used to measure the dielectric properties of the composites. Breakdown strengths were measured using a breakdown voltage tester (Xiangyu Dong, China) at a ramping rate of 200 V/s and a limit current of 5 mA; each group of composites tested nine effective points. The diameter of the upper electrode of the instrument is 25 mm, and the diameter of the lower electrode is 75 mm. The tensile properties were measured using the CMT 4000 universal testing machine in accordance with the GB/T 1040.2-2006 standard.

3 Results and discussion

The formation mechanism and SEM images of STO@MWCNTs are shown in Figure 1a. The STO colloidal particles can be easily coated on the surface of MWCNTs due to the electrostatic interaction and π - π conjugate interaction forces of MWCNTs and SDBS. After sintering at 800°C for 2 h under a nitrogen flow in a tube furnace, the STO nanoparticles can be coated on the MWCNTs. As shown in Figure 1b and c, compared with the smooth surface of pure MWCNTs, the inorganic nanoparticle coating can be clearly seen on the surface of MWCNTs, indicating that STO successfully coated the surface of MWCNTs.

As shown in Figure 2a, from the appearance of the platform at the low frequency of the conductivity curve, the composite changed from an insulator to a conductor. Given the narrow percolation threshold, the composites were transformed into a conductor at 3 wt% MWCNTs, causing difficulty in controlling the dielectric properties of composites with MWCNTs as filler. In contrast, as shown in Figure 2b, the linear correlation between AC conductivity and frequency also indicated that the composite was still an insulator and that the filler

Figure 1: (a) Mechanism of STO@MWCNT formation. SEM images of (b) MWCNTs and (c) STO@MWCNTs.

concentration did not reach the percolation threshold. When the filler content is 11 wt%, the STO@MWCNTs/PDMS composite still maintains a low AC conductivity at 100 Hz.

The frequency dependence of the dielectric properties was measured for MWCNTs/PDMS and STO@MWCNTs/PDMS composites at room temperature (Figure 3). The addition of MWCNTs in PDMS suddenly increased the dielectric loss of the composites (Figure 3b). As shown in Figure 3c and d, the composites comprising STO@MWCNTs showed high dielectric constant and low dielectric loss at low filler concentrations (<11 wt%) due to the STO shell preventing MWCNTs from being in contact with each other. As a high dielectric ceramic, STO can also effectively increase the dielectric constant of

the composites. Under a low filler loading amount of 11 wt%, the dielectric constant and dielectric loss of the STO@MWCNTs/PDMS composite is 53 and 0.1, respectively.

The breakdown strength is an important parameter for dielectric materials because it determines the operating electric field. The addition of conductive fillers inevitably and severely reduces the breakdown strength of composites. As shown in Figure 4, the MWCNTs/PDMS composites exhibited extremely low breakdown strength due to the easy contact of pure MWCNTs with each other to form the conductive path to transform the PDMS into a conductor. By contrast, the insulating ceramic layer can effectively prevent the formation of conductive paths due

Figure 2: Frequency dependence of AC conductivity of (a) MWCNTs/PDMS and (b) STO@MWCNTs/PDMS composites.

Figure 3: Frequency dependence of (a and c) dielectric constants and (b and d) dielectric loss of MWCNTs/PDMS and STO@MWCNTs/PDMS composites.

Figure 4: (a) Weibull distribution of STO@MWCNTs/PDMS. (b) Breakdown strength of MWCNTs/PDMS and STO@MWCNTs/PDMS composites. (c) Schematic diagram of the conductivity effect of the two kinds of composites.

Figure 5: SEM images of freeze-fractured surfaces of STO@MWCNTs/PDMS composites with (a) EP, (b) 3%, (c) 5%, and (d) 11 wt% filler.

to the formation of STO coating on the surface of the MWCNTs. Therefore, the composite can still maintain superior breakdown strength. Even at a filler mass fraction of 11 wt%, the STO@MWCNTs/PDMS composites still exhibited relatively high breakdown strength (3.6 kV/mm). Thus, this strategy provided a feasible method for improving the breakdown strength of the conductive filler/polymer composites.

The morphologies of STO@MWCNTs/PDMS composites were investigated through SEM (Figure 5a–c). The STO@MWCNTs revealed good dispersibility in the PDMS matrix. No evident agglomeration occurred at various STO@MWCNTs content levels. The coating of STO can

reduce the surface energy of MWCNTs, thus effectively preventing the agglomeration of MWCNTs. With the increase in STO@MWCNTs content, more MWCNTs appeared on the surface of the polymer matrix but still have better dispersion, which also provides a guarantee for the improvement of the breakdown strength of composites.

The theoretical energy storage density of linear dielectric materials can be calculated from (22):

$$U_e = 1/2 \varepsilon_0 \varepsilon_r E_b^2$$

where ε_0 is the vacuum constant, ε_r is the dielectric constant, and E_b is the breakdown strength. In our work, the breakdown strength of STO@MWCNTs/PDMS is higher

Figure 6: (a) Stress–strain curves of STO@MWCNT/PDMS composites. (b) Tensile strength and elongation at break of STO@MWCNT/PDMS composites.

than MWCNTs/PDMS but lower than pure PDMS due to the inherent properties of MWCNTs and mismatch between inorganic filler and matrix. Thus, as the mass fraction of the filler increases, the dielectric constant of STO@MWCNTs/PDMS increases but the breakdown strength decreases significantly, resulting in a limited increase in the energy storage density.

Furthermore, the typical stress–strain curves were determined to investigate the effect of different STO@MWCNTs loadings on the mechanical properties of the composites, as shown in Figure 6. The low concentration of STO@MWCNTs did not cause an excessive loss in the mechanical properties of the composites. With the increase in the filler concentration, the tensile strength of the composites initially increased and then decreased, and the elongation at break gradually decreased. At 11 wt% STO@MWCNTs, the tensile strength reached 2.85 MPa, indicating that the composite can still maintain its good mechanical properties.

4 Conclusion

A core–shell STO@MWCNT was designed as filler to study the effect of the dielectric properties of the PDMS composite. The improved dielectric performances, breakdown strength, and mechanical properties were observed. As coating, STO effectively prevents the overlap and agglomeration of MWCNTs, thereby passivating the percolation threshold of the composite. Moreover, STO significantly increases the dielectric properties of the composite as a high dielectric ceramic. In addition, the composite can still maintain superior breakdown strength and mechanical properties due to the relatively low filler concentration. The enhanced dielectric properties and tensile strength qualify STO@MWCNT/PDMS composites for application as dielectric materials in flexible and stretchable electronics.

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