Three-dimensionally ordered macroporous BaTiO₃ framework-reinforced polymer composites with improved dielectric properties

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Abstract

Polymer composites with high dielectric constants are highly desired in advanced electronic devices and the modern electrical industry. The dielectric constant of three-dimensional filler-reinforced polymer composites is usually enhanced at the expense of flexibility. Herein, barium titanate inverse opals (BT_IOs) that have three-dimensionally ordered and interconnected macropores are prepared and introduced into a poly (vinylidene fluoride) (PVDF) matrix to tailor their dielectric properties. The composite films with 30 wt% BT_IOs exhibit a dielectric constant of 18.8 at 1 kHz, showing an enhancement of 154% and 35% compared with that of pristine PVDF and their corresponding composites reinforced with barium titanate nanoparticles, respectively. Meanwhile, the dielectric loss is suppressed at 0.088. The BT_IOs/PVDF composite films also maintain good flexibility and can be freely bent. This design of three-dimensionally ordered macroporous filler-reinforced polymer composites with improved dielectric constants and good flexibility presents promising applications of dielectric materials in flexible electronics.

Keywords 3DOM · Barium titanate · Inverse opals · Polymer composites · Dielectric properties

1 Introduction

Materials with high dielectric constants are extensively explored because of their potential applications in advanced electronics and the modern electrical industry, such as in dielectric elastomer actuators, transistors, electrostatic capacitors and electrical stress control systems [1–3]. Polymer dielectric composites are expected to integrate excellent flexibility and easy processing of polymer matrixes with fillers with high dielectric constants. Various types of fillers, such as linear dielectrics [4, 5], paraelectrics [6, 7], ferroelectrics [8, 9], relaxor ferroelectrics [10], antiferroelectrics [11, 12], giant dielectric constant fillers

[13, 14] and conductive fillers [15, 16], have been introduced into polymers to tailor their dielectric properties. Their high dielectric constants usually result from two aspects. First, ceramic fillers with a high intrinsic dipole strength can enhance the effective dipole strength of polymer composites according to the effective medium theory [17]. Second, differences in dielectric constants or conductivities between matrix and fillers can induce Maxwell–Wagner–Sillars effect or equivalent microcapacitor effect [18–20].

Filler dimensions or morphologies also greatly affect the dielectric properties of polymer composites [21–23]. Hao et al. [24] introduced ultrafine barium titanate

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nanoparticles (BT_NPs) into a poly(vinylidene fluoride-co-hexafluoro propylene) (P(VDF-HFP)) polymer matrix. The 70 vol% BT_NP/P(VDF-HFP) polymer composites exhibit a dielectric constant of about 34 at 1 kHz, showing a 240% enhancement compared with that of pristine P(VDF-HFP). Given that the high dielectric constant of zero-dimensional (0D) nanofiller/polymer composites is usually obtained at high filler contents, its considerable enhancement is usually achieved at the expense of increased dielectric loss and deteriorated mechanical properties. As an alternative solution, anisotropic nanofillers are introduced into polymer dielectric composites [25–28]. Owing to the large susceptibility along the longitudinal direction of one-dimensional nanofillers and in-plane directions of two-dimensional nanofillers, anisotropic nanofillers are capable of inducing substantially higher dielectric constants at the same filler content than their 0D counterparts [29, 30]. Three-dimensional (3D) fillers show great potential in boosting the dielectric constants of polymer composites because of their continuous transmission of polarization throughout the 3D framework [31] or continuous coupling effect of interconnected adjacent filler grains [32]. Feng et al. [33] theoretically demonstrated that constructing ceramic frameworks in polymer matrixes effectively boost their dielectric constants at low filling contents.

The structures of 3D fillers have a crucial effect on the dielectric properties of polymer composites. Although several types of 3D fillers have been developed [34–37], three-dimensionally ordered macroporous (3DOM) fillers have not been utilized thus far. Herein, we prepared BT inverse opal (BT_IO) particles with 3DOM structures via a templated sol–gel method and introduced them into PVDF matrix to tailor their dielectric properties. The polymer composites with 30 wt% BT_IOs exhibit a dielectric constant of 18.8 and a dielectric loss of 0.088 at 1 kHz. Although the BT_IO/PVDF composite films exhibit a lower dielectric constant enhancement than the polymer composites in which 3D fillers exist as a whole, they maintain better flexibility. Therefore, they show promising applications in flexible electronics.

2 Materials and methods

2.1 Materials

Styrene and sodium dodecyl sulfate were purchased from Damao Chemical Reagent Factory (Tianjin, P.R. China). Acetylacetone was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd (Tianjin, P.R. China). Barium hydroxide octahydrate, tetrabutyl titanate, acetic acid, ethanol and N,N-dimethylformamide were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, P.R. China). PVDF

powders with Mw = 534,000 were purchased from Sigma-Aldrich Trading Co., LTD (Shanghai, P.R. China). Styrene was alternately washed with 0.1 M NaOH and deionized water to remove polymerization inhibitors before use.

2.2 Preparation of BT precursor

In a typical process, 0.01 mol of barium hydroxide octahydrate was added into 10 mL of acetic acid and refluxed at 60 °C. The solution was cooled to 0 °C in an ice water bath after barium hydroxide octahydrate completely dissolved. Another solution containing 0.01 mol of tetrabutyl titanate, 20 mL of ethanol and 1 mL of acetylacetone was prepared and added to the Ba-contained solution drop by drop under continuously magnetic stir. The obtained transparent yellow solution was used as BT precursor after aging for 24 h at room temperature.

2.3 Fabrication of BT_IO particles

Monodisperse polystyrene (PS) spheres were synthesized adopting an optimized version of literature techniques and assembled into artificial opal templates via a thermal-assisted colloidal assembly method [38]. BT_IO particles were fabricated via a sacrificial template method. Typically, BT precursor was dropped on the edge of opal templates. The interstices between colloidal spheres were filled with BT precursor by capillary action. After kept at room temperature for more than 6 h, the composites were calcined for 4 h in a muffle furnace to fabricate BT_IOs. BT_NPs were prepared by calcining the same precursor.

2.4 Fabrication of BT/PVDF composite films

BT fillers were dispersed in N,N-dimethylformamide by ultrasonication. Then, PVDF was added into the suspension in proportion. After mechanically stirred for 12 h, the mixture was cast on clean glass slides and dried in vacuum at 80 °C. The dried composite films were further heated at 200 °C for 10 min and then immediately quenched in ice water. Flexible BT/PVDF films were obtained after the quenched films were heated in vacuum at 80 °C to remove residual water and peeled off from the glass slides.

2.5 Characterization

Scanning electron microscopy (SEM) images were obtained using a Nova Nano SEM 450 scanning electron microscope. Optical photos were captured with a Nikon digital camera. Phase composition of the BT samples was studied by powder X-ray diffraction (XRD) analysis using a Rigaku D/MAX 2500 diffractometer with a filtered Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). Raman spectroscopy was

performed in air by using a backscattering micro-Raman spectrometer with helium–neon laser (633 nm) excitation. The dielectric properties were tested at frequency from 10^2 to 10^6 Hz with 0.5 V rms by an Agilent 4294A LCR impedance analyzer. The Au layer electrode with a diameter of 4 mm was sprayed on both sides prior to test.

3 Results and discussion

3.1 Preparation and characterization of BT_IOs

3DOM BT particles were prepared via a templated sol–gel method (Fig. 1a) [39]. PS spheres were assembled into closely packed face-centered cubic (FCC) structures on

glass substrates to form an opal template by thermally assisted self-assembly method. Subsequently, the aged BT precursor was infiltrated into the template and gradually solidified. Finally, the opal template was removed by calcination.

Monodisperse PS spheres were prepared via emulsifier-free emulsion polymerization and directly used to prepare opal templates without purification. The elaborate PS opal templates present close-packed FCC arrangements (Fig. 1b and c). The aged BT precursor was carefully infiltrated into the templates to ensure that their structures could survive. After solidification and calcination at 650 °C, the PS opals burned out and the BT particles formed an inverse structure (Fig. 1d and e). The O, Ti and Ba elements were uniformly distributed (Fig. 1f), indicating that the BT_IOs

Fig. 1 **a** Schematic showing the preparation of BT_IOs. **b** Top view and **c** cross-view of PS templates. **d** Top view and **e** cross-view of BT_IOs. **f** EDX elemental mapping of BT_IOs

were chemically homogeneous. The average diameter of the PS spheres is 440 nm, whereas the average center-to-center distance between neighboring air spheres in the obtained BT_IOs is 290 nm, showing a shrinkage factor of about 34%. The pores connecting two neighboring air spheres have a diameter of about 80 nm. Moreover, the pores are arranged in 3D in BT_IOs, as indirectly evidenced by the structural color of the BT_IO film (Fig. S1). Islands of BT_IO formed on the glass substrates because of the intensive shrinkage (Fig. S2). Consequently, BT_IOs could be easily collected by stripping from the coverslips. The 3DOM structure allowed polymer infiltration and thus the formation of dense BT_IO/PVDF composite films.

The XRD patterns of BT_IOs and BT_NPs prepared at different calcination temperatures were determined to identify their phase compositions (Fig. 2a). BT powders crystallized at temperatures above 600 °C. All samples calcined at above 600 °C contain trace amounts of impurities, which are dominated by BaSO₄ and BaCO₃ in BT_IOs and BT_NPs, respectively. In the preparation of PS spheres, the sulfur element was introduced using potassium peroxydisulfate as the initiator. As a result, BaSO₄ appears as an impurity in BT_IOs.

A comparison of two 600 °C X-ray lines reveals that the PS templates affect BT crystallization. The same trend in which high-temperature benefit crystallization is observed for both BT_NPs and BT_IOs. Notably, the splitting of reflection peak at about $2\theta = 45^\circ$, which is used to distinguish the tetragonal phase of BT from its cubic phase, is not observed for all X-ray lines. Nevertheless, the phase of the products cannot be classified as a cubic phase because of the inherent line-broadening effect resulting from the small crystal size [40, 41].

Given that the softening deformation of coverslip substrates occurred at above 650 °C, the BT_IOs used as fillers were calcined at 650 °C. For comparison, the BT_NP fillers were also obtained at 650 °C. Raman scattering was conducted to ascertain further the crystal structures of the BT fillers. On the basis of the crystallography, 10 Raman-active modes were predicted for tetragonal BT with a space group of $P4mm$; symmetry demands that cubic BTs with a space group of $Pm3m$ should be completely Raman-inactive [42]. Nevertheless, owing to the disorder of titanium in the nominally cubic BT, broad peaks at about 250 and 520 cm⁻¹ can be observed above the Curie temperature [43]. The room temperature Raman spectra of the BT fillers are shown in Fig. 2b. The band centered at 183 cm⁻¹ is assigned to the fundamental TO mode of A1 symmetry. The sharp peak at 304 cm⁻¹ is attributed to B1 mode, indicating asymmetry within the TiO₆ octahedra of BaTiO₃ on a local scale. The weak peak at 715 cm⁻¹ is related to the highest frequency LO mode with A1 symmetry [44]. Among these peaks, the peak at about 183 cm⁻¹ other than 194 cm⁻¹ distinguishes the tetragonal from the orthorhombic phase. The peaks at 304 and 715 cm⁻¹ distinguish the tetragonal phase from the cubic phase because they disappear above the Curie temperature. The strong peak at 304 cm⁻¹ suggests that the tetragonal phase is dominant in BT_NPs, but its intensity decreases in BT_IOs. These results demonstrate that the PS spheres indeed affect BT crystallization, consistent with the XRD results. Furthermore, the peaks at 984 and 1055 cm⁻¹ signify the existence of BaSO₄ and BaCO₃ in BT_IO and BT_NP, respectively.

Fig. 2 **a** XRD patterns of BT fillers calcined at different temperatures. **b** Raman spectra of BT fillers calcined at 650 °C

3.2 Morphologies and dielectric properties of BT/PVDF composite films

PVDF solution infiltrates into BT_IO particles by capillary action and gravity, forming dense and defect-free composite films after drying (Fig. 3a–h), and BT_IOs are evenly distributed in the composite films (Figs. S3 and S4). When the filling content is less than 20 wt%, the composite films exhibit smooth surfaces on both sides (Fig. 3a, d and g). As the filling content further increases, the top surfaces of BT_IO/PVDF composite films become rough (Fig. 3e and f) because the 3DOM BT_IOs stack and exceed the top film surface without confinement (Fig. 3h). Even though, the composite films exhibit excellent flexibility and can be freely bent because the 3D fillers are not a whole (Fig. 3i).

The frequency dependence of the dielectric constant and loss of BT_IOs/PVDF is presented in Fig. 4a and b, respectively. The dielectric constant of all BT_IOs/PVDF

films decreases as the frequency changes from 10^2 to 10^6 Hz. At the same frequency within this range, the dielectric constant gradually increases as the filler content increases. For example, the dielectric constant of the 30 wt% BT_IO/PVDF composite films reaches 18.8 at 1 kHz, showing a 154% enhancement compared with that of pristine PVDF (7.4), and the dielectric loss is maintained at 0.088.

For comparison, the dielectric properties of the BT_NP/PVDF composite films were also measured (Fig. 4c). The dielectric constant and loss at 1 kHz of the composite films with various filler contents are summarized (Fig. 4d). The dielectric loss shows a relatively sharp increase as the filler content increases from 15 wt% to 20 wt%. This result is attributed to the formation of a continuous network in the composite films, as depicted in Fig. 5a. BT_IOs are separately distributed when the filler content is lower than the critical value (f_c), and a continuous network forms when

Fig. 3 SEM images showing bottom surfaces of PVDF-based composite films with **a** 20 wt%, **b** 25 wt% and **c** 30 wt% BT_IOs. SEM images showing top surfaces of the PVDF-based composite films

with **d** 20 wt%, **e** 25 wt% and **f** 30 wt% BT_IOs. Cross-sectional SEM images of **g** 20 wt% and **h** 25 wt% BT_IO/PVDF composite films. (i) Digital photo of a 25 wt% BT_IO/PVDF composite film

Fig. 4 **a** Dielectric constant and **b** dielectric loss of the BT_IO/PVDF composite films with different filler contents. **c** Dielectric constant and dielectric loss of the BT_NPs/PVDF composite films with differ-

ent filler contents. **d** Comparison of measured dielectric constant and dielectric loss at 1 kHz of composite films with different fillers

Fig. 5 **a** Schematic illustration of a continuous BT_IOs network in the composite films. Schematic illustrations showing polarization behaviors of BT grains in **b** BT_NP/PVDF and **c** BT_IO/PVDF com-

posites under an applied electric field. The carmine arrows show the directions of polarization

the filler content is equal to f_c . As the filler content overcomes f_c , the BT_IO particles stack together and exceed the top film surface (Fig. 3h). The dielectric loss of the BT_NP/PVDF composite films also shows a relatively sharp increase at the filler content of 30 wt% because of filler aggregations. The difference in the critical filler contents is due to differences in bulk density (Fig. S5).

Aside from differences in dielectric loss, differences in the dielectric constants are evident. The BT_IO/PVDF composite films show higher dielectric constants than their corresponding BT_NP/PVDF composite films because of the continuous polarization coupling effect of BT_IOs. The homogeneously distributed BT_NPs exhibit rearranged but relatively random polarization directions (Fig. 5b), whereas the connected BT particles in the BT_IOs network show an aligned polarization direction under an applied electric field (Fig. 5c), thereby efficiently enhancing the dielectric constant [33]. Moreover, the difference increases as filling content increases, which can be partly ascribed to the formation of continuous networks.

Although the dielectric properties of the BT_IO/PVDF composites are improved, the results fall short of expectations. Two main reasons are responsible for this outcome. First, the as-prepared BT_IOs have a low degree of crystallinity. Second, the 3DOM structures collapse during the filler collection and composite preparation processes, resulting in relatively small filler sizes (Fig. S6).

4 Conclusion

Introducing 3DOM fillers into a polymer matrix to tailor their dielectric properties is reported for the first time in this study. Two sizes of macropores exist inside the as-obtained BT_IO fillers. The small pores connecting the neighboring large air pores enable the complete infiltration of the PVDF matrix, thereby ensuring the formation of dense composite films. The special aggregation state of the BT particles constructing BT_IOs facilitates the continuous polarization coupling effect under an applied electric field. Collectively, the BT_IO/PVDF composite films exhibit higher dielectric constants than their corresponding BT_NP/PVDF composite films, whereas the dielectric loss maintains a low value. For example, the 30 wt% BT_IO/PVDF composite films have a dielectric constant of 18.8, which is 35% higher than that of corresponding BT_NP/PVDF composite films. Meanwhile, they show excellent flexibility and can be freely bent. This work presents a novel and universal strategy for preparing 3DOM filler-reinforced polymer composites with improved dielectric properties and good flexibility. These composites show considerable potential in achieving high dielectric constant materials for wearable electronics.

5 Supplementary data

Digital photo showing structure color of as-obtained BT_IOs; Low-magnification SEM image of as-obtained BT_IOs; Element mapping of BT_IO/PVDF composite films; Digital photo of as-obtained BT_IO and BT_NP fillers; SEM image of BT_IO fillers after stripping from the coverslips.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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