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Ceramics International 38 (2012) 1071–1075

CERAMICS INTERNATIONAL

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Electrical energy density and dielectric properties of poly(vinylidene fluoride-chlorotrifluoroethylene)/$BaSrTiO_3$ nanocomposites

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Received 27 July 2011; received in revised form 13 August 2011; accepted 14 August 2011
Available online 24 August 2011

Abstract

A series of poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE))/barium strontium titanate (BST) nanocomposites were fabricated by solution casting method. The addition of BST nanoparticles could enhance both the dielectric constant and the displacement of the resultant composite significantly. The surface activation of BST nonaparticles with KH550 was confirmed as an effective way to improve the breakdown strength of the composite. The high electric displacement ($D > 15\ \mu C/cm^2$), breakdown field (>200 MV/m) and low dielectric loss in P(VDF-CTFE)/BST nanocomposites suggest that the high electrical energy density may be desirable. That indicates the potential application of this class of copolymer/ceramics nanocomposites for high energy storage components.

Keywords: B. Nanocomposites; C. Dielectric properties; P(VDF-CTFE); $(Ba_{0.7}Sr_{0.3})TiO_3$; Energy density

1. Introduction

Poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) have attracted considerable research interests in past decades due to their great potential in advanced applications such as actuators, memories, transducers and sensors [1–3]. It has been reported that the ferroelectric PVDF or P(VDF-TrFE) modified by incorporating certain content of chlorotrifluoride ethylene (CTFE) or chlorodifluoride ethylene (CDFE or CFE) as defects exhibits large polarization and electrostrictive strain response [4,5]. More recently, it has been found that the addition of comonomer defects may also turn their crystal phase from high polar β-phase into α- or γ-phase with lower polarity [6]. As a result, the polarization saturation electric field of these modified copolymers was significantly enhanced while the remnant polarization was dramatically reduced. Therefore, the ferroelectric polymers have been turned into ferroelectric elastomers characterized with a much slimmer displacement–electric field (D–E) hysteresis loops. That means the electric energy stored in the dielectrics could be released freely as the dielectric field removed and they are highly expected to be used in high pulse capacitors for energy storage purpose. For example, the saturation electric field of P(VDF-TrFE-CFE) was reported to be extended to over 500 MV/m with a discharged energy density of 13 J/cm^3 [7]. Moreover, the stretched P(VDF-CTFE) films in low polar α crystal phase were reported to be applied under electric field over 650 MV/m with an energy density of 25 J/cm^3 [8]. That means the P(VDF-CTFE) is more desirable for energy storage purpose compared to P(VDF-TrFE-CTFE) terpolymer.

Ceramic particles, such as barium titanate ($BaTiO_3$), lead zirconate titanate (PZT) and copper calcium titanate (CCTO), have been widely applied as fillers to prepare polymer/ceramic composite with enhanced dielectric constant as well as high energy density as indicated in the formula of $U_e = 1/2\varepsilon_0\varepsilon_r E^2$ [9–11]. However, the addition of large quantity of ceramics into the polymer matrix usually resulted into the dramatic decrease of the breakdown electric filed (E_b) of the composites although it was rarely mentioned. For example, J. Robertson's group reported that the acrylic/$BaTiO_3$ composites exhibit a relatively high dielectric constants ($\varepsilon_r > 40$) but a rather low breakdown

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doi:10.1016/j.ceramint.2011.08.033

electric field ($E_b < 8$ MV/m) [12]. Therefore, the energy density of the resultant composite was not significantly improved as expected. In addition, the energy density of composites calculated from above formula may be overestimated since the D–E loops of many composites are not in linear against applied electric field, especially for the composites containing ferroelectric matrix or fillers characterized with a rather fat hysteresis loops as indicated in the literature [7]. Therefore, the discharged energy density of poly(vinylidene-hextrafluoropropylene)/TiO_2 composite should be much lower than the one (7 J/cm^3) calculated with the formula of $U_e = 1/2\varepsilon_0\varepsilon_r E^2$ in the literature [13]. It has been widely accepted that the low energy density of composites is mainly attributed to their low breakdown strength, which is closely related to the weak interface between the organic polymer and inorganic compounds induced by their poor compatibilities.

In the present study, the dielectric and energy storage properties of P(VDF-CTFE)/BST composites were carefully studied. The high-dielectric-constant barium strontium titanate (BST) nanoparticles with high surface activity were synthesized *via* a wet-chemical route followed by surface modification with a silane coupling agent (KH550) to improve the compatibility between ceramics and polymer [14,15]. P(VDF-CTFE) (94/6 in molar ratio) and surface modified BST nanoparticles were utilized to fabricate the composite films by a solution casting method. Thermal treatment (quenching the composite films from 200 °C into ice-water bath) was employed to improve E_b of the composites [16].

2. Experimental

BST ($(Ba_{0.7}Sr_{0.3})TiO_3$) nanoparticles were synthesized by a wet-chemical method as follows. An aqueous solution of citric acid (0.1 mol) and titanium (IV) isopropoxide (0.1 mol) was prepared under vigorous stirring. Meanwhile, another aqueous solution of citric acid (0.1 mol) in the mixture of barium acetate (0.07 mol) and strontium acetate (0.03 mol) was prepared and kept in another container. Immediately, these two solutions were mixed and followed by continuous stirring for 3 h. Ethyl glycol was added to the obtained solution, and the mixture was stirred for another 4 h until a clear gel was obtained before diethylene triamine was added into the solution to neutralize its pH to 7. The dry gel precursor was obtained by drying the resultant solution at a temperature of 50–70 °C. BST nanoparticles were prepared *via* decomposing the organic compounds in a muffle furnace at 400 °C for 5 h and 800 °C for 2 h.

BST nanoparticles (8 g) were dispersed in a water–isopropanol solution (45/55, vol%, 200 ml) ultrasonically for about 2 h before KH550 (5 g) and diluted hydrochloric acid were added to adjust the pH value until pH 3–4.The resultant mixture was stirred in nitrogen atmosphere for 1 h and the ceramic particles was then collected *via* filtration and rinsed with ethanol twice. The surface activated BST nanoparticles were dried at 80 °C for 12 h and ground to fine powers.

P(VDF-CTFE) (94/6 in molar ratio) was purchased from Solvay Solex Co. and utilized as the matrix without further purification, which was dissolved in dimethylformamide (DMF) completely before modified BST particles were introduced and dispersed in the solution. The resultant composites with alternated mass fractions of BST of 0 wt%, 10 wt%, 20 wt% and 30 wt% were obtained and marked as S0, S1, S2 and S3, respectively. The mixture of P(VDF-CTFE) and BST nanoparticles were cast onto the quartz slide followed by evaporating solvents completely at 70 °C under reduced pressure for 3 h. After maintained at 200 °C for 30 min, the obtained films with the thickness about 20 μm were immediately quenched in ice-water bath (0 °C) [16].

Transmission electron microscope (TEM-4000EX, JEOL, Japan) and field emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Japan) were applied to analyze the BST nanoparticles. XRD (RIGAKU D/MAX-2400, Rigaku Industrial Corporation, Japan) was performed to verify the crystal structures in the films. The wavelength of the X-ray was 1.542 Å (Cu Kα radiation, 40 kV and 100 mA) and the scanning velocity was 10°/min. Platinum electrodes (thickness = 80 nm) were sputtered on both surfaces of the composite films on a JEOL JFC-1600 Auto fine coater (Japan) for electric measurements. Dielectric properties were measured at different frequencies using a HP (Agilent-4294A) LCR meter. The polarization hysteresis loops were determined using a TF Analyzer 2000 (aixACCT, Germany) ferroelectric test system, in which an electric field with a triangular wave form at a frequency of 10 Hz was employed.

3. Results and discussion

The XRD results of BST nanoparticles are presented in Fig. 1, and the main peaks at about 31.8°, 39.2°, 45.5° and 56.6° correspond to the diffraction of plane (1 0 0), (1 1 1), (2 0 1) and (2 1 1), respectively. These peaks may confirm the tetragonal structure of $B_{0.7}Sr_{0.3}TiO_3$. According to results reported in the literature, BST particles in this crystal structure possess a higher dielectric constant than that in the other crystal forms [14].

The morphology of BST nanoparticles was characterized with TEM as presented in Fig. 2. The average diameter of the BST particles is about 50 nm. The EDS pattern and diffraction circles could also confirm the BST phase.

The morphologies of fractured surface of P(VDF-CTFE)/BST (70/30, wt%) composite films containing raw BST and KH550 modified BST were shown in Fig. 3(a) and (b), respectively. Apparently, the interface connectivity between the copolymer and BST nanoparticles (coupled by KH550 (Fig. 3(a)) has been improved compared to the one containing uncoated BST nanoparticles (Fig. 3(b)). The silane coupling agent can be hydrolyzed to form Si–OH bonds on one side of the molecule chain, which could be chemically anchored on the BST nanoparticles *via* reacting with the –OH bonds on the nanoparticles surface. Furthermore, amidogen on the other side of the KH550 molecule chain may catalyze the elimination of HCl or HF from P(VDF-CTFE)) and involve the following

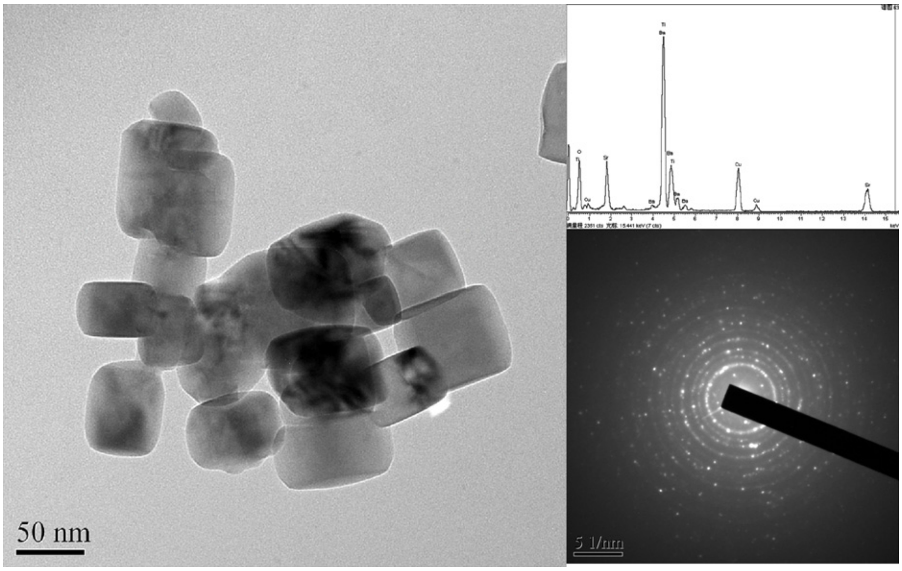

Fig. 1. The TEM micrographs of BST nanoparticles.

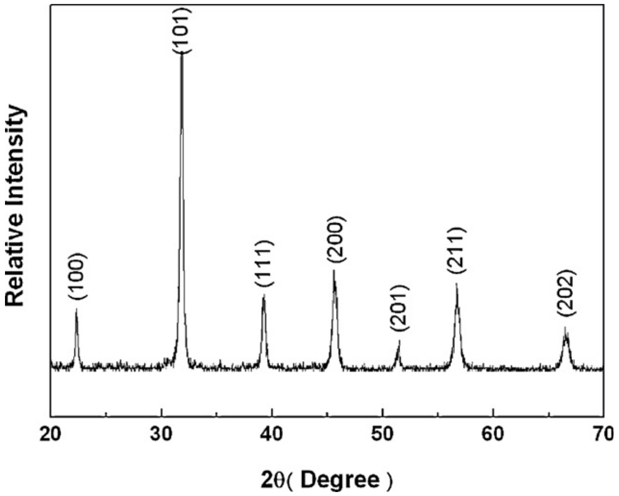

Fig. 2. X-ray diffraction pattern (XRD) of BST nanoparticles.

addition reaction with C═C bonds obtained. As a result, silane coupling agent acting as a bridge here could meliorate the interface between the ceramic nanoparticles and fluoropolymer matrix.

The dielectric constant of the pure copolymer and composites with different content of BST nanoparticles as a function of frequency was presented in Fig. 4. ε_r of all the composites and copolymer films decrease as a function of frequency ranging from 100 Hz to 10 MHz (Fig. 4(a)), which is related to the reduction of the dipolar contribution at high frequencies [17]. Furthermore, ε_r increase continuously as more BST nanoparticles are introduced and reach 82 at 100 Hz in composite S3 with 30 wt% BST, which are mainly attributed to the introduction of BST nanoparticles with high dielectric constant. In addition, dielectric loss ($\tan\delta$) curves of the copolymer and nanocomposites are both in V-shaped against the rising frequency as shown in Fig. 4(b). The decrease of $\tan\delta$ under lower electric frequency could be attributed to the response of crystal phase in polymer matrix [5]. Furthermore, $\tan\delta$ of nanocomposites increase as the contents of BST particles at low frequency. The major reason may be the increasing interface induced by the higher addition of BST nanoparticles, and that the large interface area in the nanocomposites would produce Maxwell–Wagner–Sillars (MWS) interfacial polarization at low frequency and lead to an ‘interaction zone’ with the Gouy–Chapman diffuse layer,

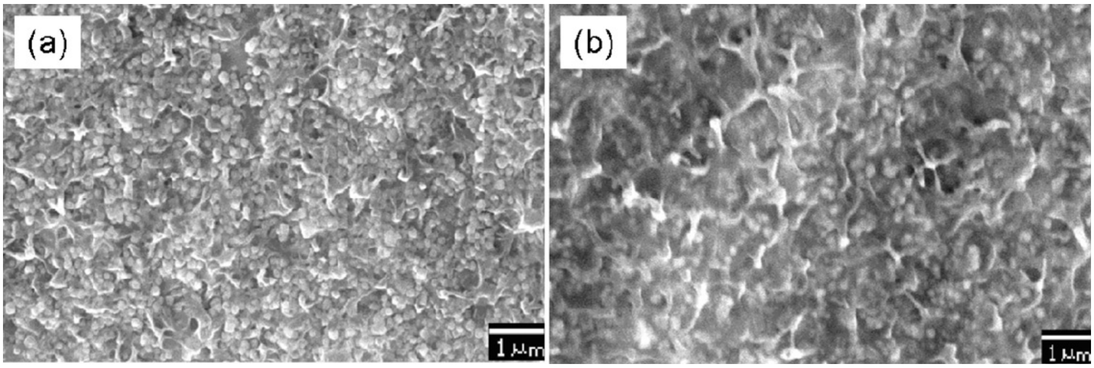

Fig. 3. FESEM micrographs of fractured surface of nanocomposite films: (a) P(VDF-CTFE)/BST nanocomposites with BST coupled by KH550 and (b) P(VDF-CTFE)/BST nanocomposites with raw BST.

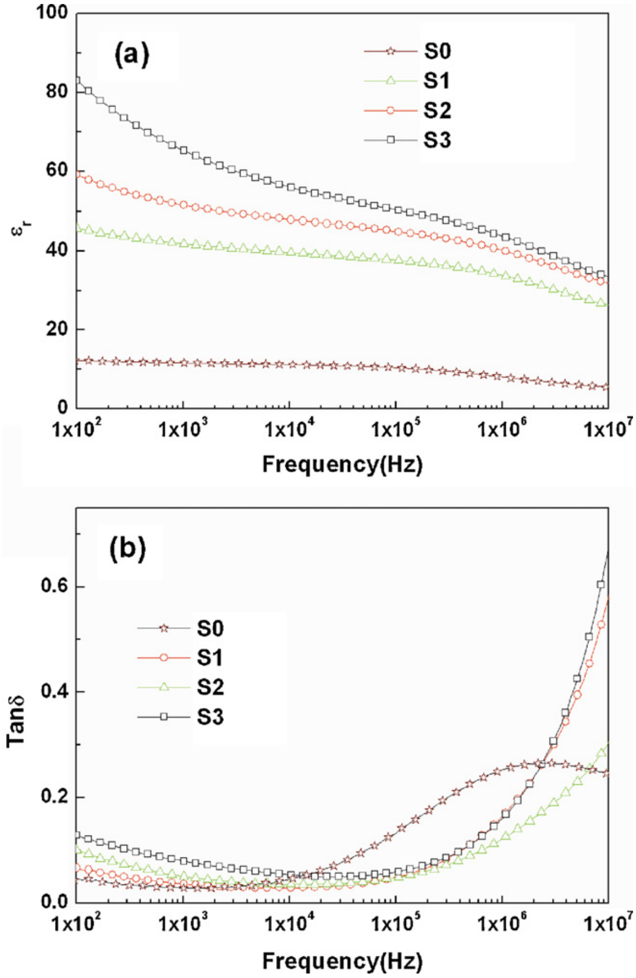

Fig. 4. Dielectric properties of P(VDF-CTFE) and various P(VDF-CTFE)/BST nanocomposites: (a) dielectric constants and (b) dielectric loss.

thereby greatly affecting polarization and dielectric responses of the polymer matrix [13]. However, the continuously improved tan δ with the rising frequency is believed to be related to not only the amorphous phase of polymer matrix but also the relaxations of permanent reorientable dipoles in ceramics, therefore, the profile of tan δ as a function of frequency is more consistent with the profile of neat BST ceramic as reported [18]. The relatively low dielectric loss of composites at low frequency also suggests that the contribution of interface zone is rather low, which may be attributed to the better compatibility between the modified BST and P(VDF-CTFE). That means the interface shows a significant influence on the dielectric properties of the composite with the surface of the BST is coated.

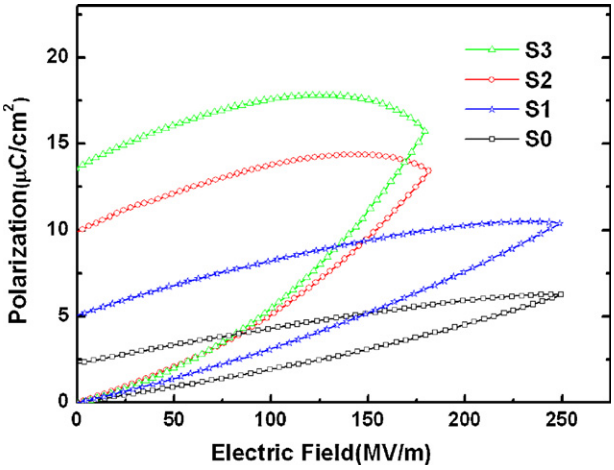

Fig. 5. D–E hysteresis of loops P(VDF-CTFE)/BST nanocomposites with raw BST and BST coupled by KH550 under unipolar electric field.

The D–E hysteresis loops of the composite films under unipolar electric field have been obtained from a ferroelectric test system, as illustrated in Fig. 5. The saturated polarization of the composite films increases with the addition of BST particles, and reaches a maximum value of 18 μC/cm^2 in BST 30 wt% film. That means the addition of high-dielectric-constant BST nanoparticles could effectively improve the electric displacement of the composites, since the saturated displacement of pure P(VDF-CTFE) has been reported to be less than 13 μC/cm^2. However, with the addition of BST nanoparticles, the electric strength decrease from 250 MV/m of pure P(VDF-CTFE) to 180 MV/m of the composite with 30 wt% BST nanoparticles. In addition, the remnant polarization of the D–E loops is improved as the increase of BST fillers as well. That is mainly caused by the heterogeneous interface formed by the addition of BST, even though the BST surface is modified with KH550. However, the composite containing 10 wt% of KH550 modified BST exhibits higher maximum polarization but lower remnant polarization than that filled with the same content of uncoated BST as shown in Fig. 6. That strongly suggests that the surface modification could effectively reduce the polarization contribution of interface zone between the polymer matrix and ceramic fillers.

Discharged energy density (U_e) is one of the most important properties of the material for the energy storage application [8]. For composite dielectrics with nonlinear and fatty displacement–electric field loops, U_e should be obtained from the integration of the discharging circle of the D–E loops instead of calculated from the formula of $U_e = 1/2\varepsilon_0\varepsilon_r E^2$ directly since U_e

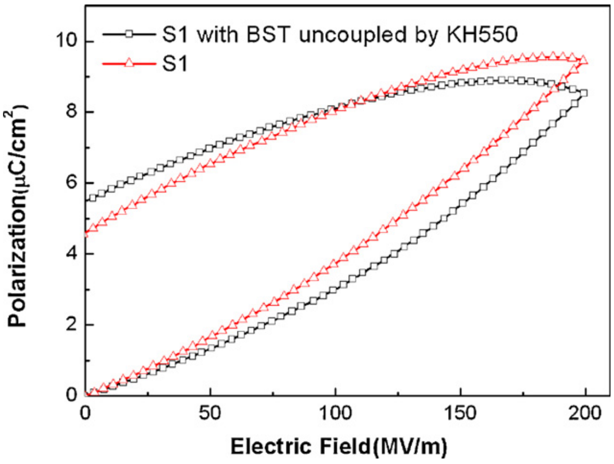

Fig. 6. D–E hysteresis of loops of P(VDF-CTFE) and various P(VDF-CTFE)/BST nanocomposites under unipolar electric field.

Table 1
Electric and energy properties of P(VDF-CTFE) samples.

Samples	Mass fraction of BST (%)	E_b [a] (MV/m)	U_e [b] (J/cm^3)	U_e [c] (J/cm^3)
S0	0	250	3.9	4.1
S1	10	250	6.5	12.5
S2	20	180	2.1	9.6
S3	30	180	1.8	11.8

[a] Breakdown electric field.

[b] Discharged energy density of the samples.

[c] Energy density of the samples calculated from the formula $U_e = 1/2\varepsilon_0\varepsilon_r E^2$ at a frequency of 100 Hz.

obtained from the latter method would be overestimated. The U_e values and the corresponding breakdown electric field of all the composites with different content of BST nanoparticles are listed in Table 1. In pure polymer, U_e is 3.9 J/cm^3 under the electric field of 250 MV/m. The composite film with 10 wt% ceramic has an energy density as high as 6.5 J/cm^3 under the same electric field. For the composite with 30 wt% BST, however, the U_e value decreases to 1.9 J/cm^3 since the breakdown electric field is reduced to 180 MV/m. Meanwhile, as shown in Fig. 5, the introduction of BST improves saturation displacements apparently, whereas it enhances remnant ones as well, which indicates more stored energy could not be discharged. Furthermore, U_e of all the composites calculated from the formula of $U_e = 1/2\varepsilon_0\varepsilon_r E^2$ were listed in Table 1 as well. Apparently, the U_e calculated from $U_e = 1/2\varepsilon_0\varepsilon_r E^2$ is much higher than that obtained from the discharging circle of D–E loops. That confirms the formula is unable to response the effective energy storage properties of the dielectric materials.

4. Conclusions

BST ceramic nanoparticles were synthesized by wet-chemical route and surface modified with silane coupling agent. A more favorable interface between the copolymer and surface activated nanoparticles was obtained than that filled with neat BST nanoparticles. Therefore, a large polarization and high breakdown electric field in the P(VDF-CTFE)/BST composites had been observed. High discharged energy density of 6.5 J/cm^3 at a breakdown field of 250 MV/m was obtained in the composite film with 10 wt% BST nanoparticles, which makes them attractive for high energy density capacitors and electric energy storage devices. The results also suggest that the energy storage ability of the composites could be improved by increasing the interface compatibility between the fillers and polymer matrix.

Acknowledgements

This work was supported by National Basic Research Program of China (973 Program) No. 2009CB623306 and the National Nature Science foundation of China-NSAF (Grant Nos. 10976022 and 50903065), SRF for ROCS, SEM, Program for New Century Excellent Talents in University, and the Fundamental Research Funds for the Central Universities.

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