Core-shell like structured barium zirconium titanate-barium calcium titanate–poly(methyl methacrylate) nanocomposites for dielectric energy storage capacitors

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Abstract

Core-shell like structured barium zirconium titanate-barium calcium titanate-poly(methyl methacrylate) [(Ba_{0.94}Ca_{0.06})(Zr_{0.16}Ti_{0.84})O₃-PMMA] nanocomposites were prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) of methyl methacrylate (MMA) from the surface of BZT-BCT nanoparticles. X-ray diffraction patterns of pure polymer and BZT-BCT nanoparticles revealed their amorphous and polycrystalline natures respectively. Fourier transform infrared spectroscopy confirmed the grafting of the PMMA shell on the surface of the BZT-BCT nanoparticles cores. Transmission electron microscopy (TEM) results revealed that BZT-BCT nanoparticles were covered by a very thin layer of PMMA forming a core-shell like structure and thermogravimetric analysis results showed that the grafted BZT-BCT-PMMA nanoparticles consist of ~80.1% PMMA by weight. Polymer grafted BZT-BCT nanocomposite thick films (~10 μm) have shown an improved dielectric constant (ε~56), a high breakdown field strength (~3 MV/cm) and high-energy storage density ~22.5 J/cm³. The improved electrical properties of core-shell like structured BZT-BCT-PMMA nanocomposites were attributed to improved nanoparticle dispersion and enhanced interfacial polarization due to the covalent linkage between polymer and nanoparticle interface. Mechanically stable and homogeneous composite films were obtained using the surface grafted BZT-BCT ceramic nanoparticles.

Keywords: Atom transfer radical polymerization, dielectrics, energy storage, poly(methyl methacrylate), nanocomposites, capacitors

1. Introduction

Ceramic materials with high dielectric permittivity and low dielectric losses have attracted attention because of their important applications in the electrical and electronic industries. In particular, perovskite based ceramic materials such as barium titanate, BaTiO_3 (BTO), and lead zirconium titanate, PbZrTiO_3 , (PZT) etc., are widely used in capacitors due to their excellent dielectric properties. For next-generation capacitive electrical energy storage applications, materials with high dielectric permittivity, low dielectric loss, and high dielectric breakdown strength (DBS) are essential for high gravimetric energy storage capacity. High-energy density storage capacitors, by definition, store more energy per unit volume than common capacitors. These capacitors play a key role in stationary power systems, mobile electronic devices, hybrid electric vehicles, and pulsed power applications due to their reliability and fast charge-discharge characteristics¹. Conventional ceramics have excellent dielectric properties (high dielectric permittivity and low dielectric loss). And these high dielectric constant dielectric materials are widely used in energy storage devices applications. However, their low DBS limits the energy storage density and performance of the capacitor, which is detrimental in meeting the high energy density capacitor functional requirements². Polymeric dielectric materials on the other hand, have some advantages over the traditional electroactive ceramics, e.g., low cost, high mechanical elasticity, high electrical breakdown strength, ease of processing in large areas/volumes, and self-healing ability³. However, most dielectric polymers possess relatively low dielectric constants ranging from 2 to 12⁴.

An effective alternative approach is to fabricate flexible polymer composites by combining ceramic nanoparticles and polymers to leverage their complementary properties. Over the past few years, many researchers worldwide have focused on developing polymer-based nanocomposites filled with high dielectric permittivity ceramic nanoparticles, in order to combine the high dielectric permittivity of ceramics and the high breakdown strength of polymers. However, introducing ceramic nanoparticles into a polymer matrix by a simple solvent mixing often causes a drastic decrease in dielectric breakdown strength (DBS) which offsets the advantages offered by the improved dielectric permittivity⁵. The decrease of DBS in

polymer/nanoparticle composites when compared with pure polymer's DBS is attributed to the agglomeration of ceramic nanoparticles, and generation of pores or voids that lead to charge accumulation and subsequent dielectric breakdown within the composite⁵.

Accumulated energy storage density or volumetric energy density (E_d in J/cm³) in linear dielectrics is determined by dielectric constant (ϵ), permittivity of free space (ϵ_0) and breakdown strength (E_b). E_d has a linear relationship with dielectric constant (ϵ) and quadratic dependence on the electric field (E_b) as shown in the following equation (1):

$$E_d = \int_0^{P_{max}} E_b dP = \frac{1}{2} \epsilon_0 \epsilon E_b^2 \quad (1)$$

To obtain higher energy densities both high dielectric permittivity and high breakdown strength are required. However, a two-fold increase in the breakdown strength can increase the overall energy density by four-fold. The quadratic dependence has inspired numerous efforts in the past few years to combine polymers exhibiting high dielectric breakdown strength with ceramic nanoparticles of high dielectric constant to improve the electrical energy storage density⁶. Volumetric energy storage density is the key factor for a dielectric capacitor; it denotes the amount of energy stored in the device and also determines the performance of the capacitor.

When compared to micron-sized ceramic particles, nanoparticles have shown improved dielectric properties. The enhanced dielectric properties of nano-sized particles have been attributed to reduced interfacial polarization and lower nanoparticle agglomeration⁷. Also, adding nano-sized TiO₂ as an additive as opposed to micron-sized TiO₂ has shown to improve dielectric properties of ceramic nanoparticles. The incorporation of nanoparticles results in reduced porosity and leads to a random close-packed microstructure in the final composite⁸. Furthermore, ceramic-polymer nanocomposites offer several very important processing advantages including mechanical flexibility and the ability to be easily molded into customized shapes; both features make them attractive materials for use in low cost, compact electrical and electronics devices.

There are various types of mixing processes that were explored to make flexible polymer-ceramic nanocomposites materials for electrical energy storage applications, which include

conventional mixing and covalently grafting of polymers from ceramic particles. In conventional mixing process, the homogeneous dispersion of nanoparticles in polymer matrices is achieved by tuning the surface energies of nanoparticles⁹. Surface hydroxylation of nanoparticles is another approach that was utilized to make nanoparticles disperse better in the polymer matrix⁵. Many other research efforts have also been reported for improving nanoparticles dispersion, such as surface modification of nanoparticles by organic molecules such as silanes¹⁰, phosphonic acid¹¹, and ethylene diamine¹²; surface initiated in-situ polymerization techniques¹³; and nanocomposite hybrid filler mixtures^{9b,14}. To improve the interfacial compatibility and enhance the dielectric properties, surface modification of fillers by covalent polymer grafting is the most effective way to achieve homogenous composites¹⁵. Using a surface grafting technique, polymer chains can be chemically grown from the surface of ceramic nanoparticles, which in turn strengthens the interactions between inorganic ceramic fillers and the polymer matrix, resulting in better dispersion of the ceramic filler and ultimately decreases the interfacial defects. With the increased scope of controlled radical polymerization (CRP) techniques, the design and synthesis of high permittivity core-shell structured hybrid nanoparticles, in which ceramic cores are covalently grafted with polymer chains, has become an appealing route to resolve the interfacial incompatibility between fillers and matrix and can yield improved composites for high energy storage capacitors¹⁵⁻¹⁶.

Herein, we report the synthesis, physical characterization, dielectric evaluation, and energy storage properties of core-shell structured PMMA grafted BZT-BCT nanocomposite prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) of MMA monomer from the surface of $[(\text{Ba}_{0.94}\text{Ca}_{0.06})(\text{Zr}_{0.16}\text{Ti}_{0.84})\text{O}_3]$ (BZT-BCT) nanoparticles.

Experimental details

Materials

Methyl methacrylate (MMA, 99%, Aldrich) was purified by passing through basic alumina. Copper (I) bromide (CuBr, 98%, Sigma-Aldrich) was purified by successively washing with glacial acetic acid, ethanol, and ethyl ether followed by drying under vacuum at room temperature. 4,4'-Dinonyl-2,2'-dipyridine (DNBP, 97%, Aldrich), *p*-toluene sulfonyl chloride (PTSC, 97%, Sigma Aldrich), 2-(4-chlorosulfonylphenyl) ethyl trichlorosilane (CTC, 50% in

methylene chloride, Gelest), and other reagents were used as received unless otherwise mentioned.

Perovskite crystalline structured BZT-BCT nanoparticles (<100 nm) were synthesized using sol-gel synthesis technique¹⁷. The dielectric, ferroelectric and energy storage properties of BZT-BCT ceramic nanoparticles were reported elsewhere¹⁷. Functionalization of BZT-BCT nanoparticles by grafting PMMA chains was carried out by surface-initiated atom transfer radical polymerization (SI-ATRP)¹⁸. The grafting of PMMA onto the BZT-BCT nanoparticles (Scheme 1) was carried out using a similar approach as that reported for the PGMA grafting on BaTiO₃ nanoparticles (see supporting information for detailed grafting and thin film preparation)^{13f}.

Preparation of free polymer and polymer nanocomposite films

Four films were prepared and characterized (F1-F4). The solutions were prepared by mixing the components into a DMF solution (formulations described below). Each formulation was then stirred for 1 h to insure the formation of stable suspensions. The suspensions were poured onto a copper substrate, kept on hot plate for 1 h at 100° C for solvent evaporation. Finally pure polymer and polymer-nanocomposite thin films with a thickness of 10-20 µm were obtained.

Film 1: PMMA thin film made purely from the PMMA free polymer (that was produced by PTSC reaction with MMA), and used as a polymer only control.

Film 2: Grafted nanoparticle film was prepared from PMMA grafted BZT-BCT (82 % polymer and 18% BZT-BCT by weight) without any additional free polymer. From the TGA results, it can be observed that the final nanocomposite contains 82% polymer (soft material) and 18% BZT-BCT (hard material)

Film 3: To draw a direct comparison and to find out the effect grafting the polymers on to the surface of the nanoparticle compared with a simple physical mixing of free polymer to the nanoparticles (F4), the following film composition was prepared. Grafted nanoparticle composite and a small amount of free polymer were utilized to increase the polymer percentage to 90% from 82% (grafted polymer material). This was achieved by adding 16 mg of free PMMA polymer to 20 mg of grafted nanocomposite. (In the 20 mg grafted nanocomposite film consists of 16.4 mg of polymer and 3.6 mg of ceramic nanoparticles. By adding 16 mg of free polymer,

the final polymer composition in the film is 32.4 mg and final ceramic composition in the film is 3.6 mg. In the overall 36 mg of nanocomposite, 3.6 mg (10%) is ceramic nanoparticles and the rest 32.4 mg (90%) is polymer which is analogous to the Film F4 with respect to the same amount of polymer to nanoparticle ratio.

Film F4: A blended composite made from 90% free PMMA polymer and 10% un-grafted BZT-BCT (without surface grafted polymer), and used as a control for simple mixing of nanoparticles and free polymer.

Characterization Techniques

In order to evaluate crystalline structure, the X-ray diffraction (XRD) profiles of four polymer/nanoparticle films investigated: 1) the free polymer PMMA alone (film F1), 2) PMMA grafted BZT-BCT (82% polymer and 18% BZT-BCT) (film F2), 3) a 90% polymer by total weight blend consisting of 44.4% free PMMA and 55.6% PMMA-grafted BZT-BCT (which contains, 44.4% free polymer by weight and an additional 45.6% grafted polymer by weight, for a total polymer content of 90% and a total inorganic BZT-BCT content of 10%) (film F3), and 4) a 90% PMMA free polymer with 10% unmodified BZT-BCT blend (film F4), and BZT-BCT ceramic nanoparticles were recorded using Cu K α radiation from a highly stabilized and automated Rigaku X-ray generator operated at 40kV and 40mA. The XRD data were recorded at a step size 0.02 and step scan 1°/min, for the entire angular range 10°–80°. Fourier transform infrared spectroscopy (FT-IR, PerkinElmer spectrometer) was used to study the functional groups of PMMA before and after surface initiation. Thermogravimetric analysis (TGA) data was acquired using TA Instruments TGA 2950 Thermogravimetric Analyzer with heating rate of 20 °C per minute under N₂ atmosphere. Data was processed using TA Instruments Universal Analysis software. Transmission electron (TEM) microscopy images were taken with a FEI G2 F30 Tecnai TEM operated at 200 kV.

Size exclusion chromatography was carried out on Waters model 1500 series pump (Milford, MA) with three-column series from Polymer Laboratories, consisting of PLgel 5 μ m Mixed D (300 $\times$ 7.5 mm²) and PLgel 5 μ m 500 Å (300 $\times$ 7.5 mm²) and PLgel 5 μ m 50 Å (300 $\times$ 7.5 mm²) columns. The system was fitted with a Model 2487 differential refractometer detector. THF was used as mobile phase (1 mL/min flow rate). The calculated molecular weight was based on

calibration using linear polystyrene standards. Data was collected and processed using Precision Acquire software. The Fourier transform infrared (FTIR) spectroscopy was performed using a NEXUS 670 FT-IR SEP. The analyte was mixed with KBr and ground into a fine powder and compacted into a pellet by applying pressure.

Dielectric characterization of the samples was conducted by Broadband Dielectric Spectroscopy (DBS) in the frequency range of 100 Hz to 1 MHz using a HP4284A inductance–capacitance–resistance (LCR) meter by using copper foil as bottom electrode and silver paste as top electrode for these films. Electrical breakdown voltage of the capacitor metal-insulator-metal (MIM) configuration was measured at room temperature using Trek (10 kV) high voltage amplifier.

Results and discussion

Crystal structure and FT-IR spectra

Figure 1 shows the room-temperature XRD patterns for films F1-F4 along with pure BZT-BCT ceramic nanoparticles with angle 2θ (degree) ranging from 20° to 80° . It is evident that all of the sintered ceramics were crystallized into a single-phase perovskite structure. The diffraction peaks of the BZT-BCT were indexed to the tetragonal crystal structure with space group ($P4mm$) in agreement with the respective Joint Committee on Powder Diffraction Standards (JCPDS) card number: 05-0626 [Joint Committee on Powder Diffraction Standards (JCPDS) card no 05-0626]. XRD diffraction pattern for pure PMMA is also shown in Fig.1. Pure PMMA (film-F1) shows a predominant and broad characteristic peaks, with a maximum at $2\theta \sim 15.5^\circ$ and along with other peaks 29.43° , 41° , 51.37° . These broad peaks indicate the amorphous nature of the polymer. XRD patterns are in agreement with the respective Joint Committee on Powder Diffraction Standards (JCPDS) card no 13-0835. For all the polymer-nanocomposites films (F2-F4), the high intensity of Cu substrate suppressed the peak intensity of BZT-BCT nanoparticles.

In the present work, 2-(4-chlorosulfonylphenyl) ethyl trichlorosilane (CTCS) coupling agent was immobilized onto the nanoparticles to provide graft-able surface functionalities. CTCS attaches to the nanoparticles surface by hydrolysis of the chlorosilyl functionality to form the Si–O–Si covalent bonds with inorganic surfaces, such as glass^{18b}. The chlorosulfonylphenyl group ($-\text{Ph}-\text{SO}_2\text{Cl}$) was selected because it is one of the best initiating groups for ATRP¹⁹. As shown in Fig. 2 (a), the FTIR spectrum of pristine BZT-BCT ceramic nanoparticles shows only three

absorption bands at 3420 cm^{-1} , 1437 cm^{-1} and 581 cm^{-1} , a broad absorption band representing some -OH groups that are present on the surface of BZT-BCT, the stretching vibration of -CO_3^{2-} from the residual metal CO_3 from the starting materials and the vibration mode of a metal–dioxo bridge, respectively²⁰.

Due to the native presence of -OH groups on the surface of BZT-BCT, the ATRP initiating sites could be introduced by the reaction of CTCS with residual surface -OH groups. The presence of absorption band at 1115 cm^{-1} (Si-O-particle) in the FTIR spectrum of BZT-BCT-CTCS (Fig. 2 b) suggested that the silane was successfully introduced onto the surface of BaTiO_3 . The absorption bands at 1374 cm^{-1} (the S=O groups) were clearly detected, providing further indication that CTCS was successfully grafted onto the surface of BaTiO_3 . However, the absorption band at $\sim 544\text{ cm}^{-1}$ (the S-Cl stretching) was completely masked by strong metal–dioxo bridge absorbance. The Fourier transform infrared (FTIR) spectra of the pure PMMA (F1), and surface initiated ATRP PMMA grafted BZT-BCT nanocomposites (F2) are shown in the wave number ranging from 400 to 4000 cm^{-1} (shown in Fig.2). The characteristic absorption band at around 1727 cm^{-1} due to strong ester carbonyl signal of PMMA (Fig. 2 d) is also present in PMMA grafted BZT-BCT nanocomposites (Fig. 2 c), but this band is completely absent in in the FTIR spectrum of BZT-BCT-CTCS (Fig. 2 b) before graft polymerization of MMA, indicating the PMMA chains are grafted onto BZT-BCT nanoparticles. The presence of grafted PMMA onto BZT-BCT nanoparticles due to strong ester carbonyl signals (1730 cm^{-1})²¹ of PMMA (Fig. 2 d) is consistent with a substantial weight loss of TGA spectrum (Fig. 3 c) of PMMA grafted BZT-BCT and complete coverage BZT-BCT nanoparticles PMMA in the of the TEM images of PMMA grafted BZT-BCT (Fig. 4 c).

Thermal Gravimetric Analysis (TGA)

TGA measurements (Fig. 3) also confirmed that immobilization of ATRP initiating sites onto BZT-BCT. Pristine BZT-BCT nanoparticles (Fig. 3 (a)) shows about 1.5 % mass loss at $700\text{ }^\circ\text{C}$ that might be due to the adsorbed moisture and surface–OH groups. The TGA curve of BZT-BCT-CTCS nanoparticles (Fig. 2 (b)) shows an additional mass loss (5.5%) at $700\text{ }^\circ\text{C}$ as compared to the BZT-BCT, providing further evidence that ATRP initiating sites were immobilized onto nanoparticles successfully. TGA was most useful in quantifying the mass of

PMMA grafted onto the BZT-BCT nanoparticles. After the grafting reaction, BZT-BCT-g-PMMA exhibited a weight loss of 80.1% upon heating to 700 °C (Fig. 3c). The majority of the mass loss occurred between 450 °C and 505 °C, with an onset of 220 °C and an inflection point of 480 °C, similar to what is observed with pure PMMA (onset at 325, inflection point at 415 °C). This can be interpreted as grafting sufficient PMMA onto the surface of the nanoparticles to account for ~ 80% of the total weight of the BZT-BCT-g-PMMA.

Transmission Electron Microscopy (TEM)

Morphological characterization and surface structure of PMMA grafted BZT-BCT nanoparticles were analyzed by TEM to directly observe the nanoscale behavior of grafted nanoparticles. From Fig. 4 it was clear that the average dimensions of nanoparticles were around 50 nm and there was no aggregation among the particles. After the reaction of nanoparticles with CTCS, there is almost no change in the morphology; however, the particles have been aggregated to some extent during their reaction with CTCS. Similarly, after the graft polymerization of MMA, the PMMA grafted BZT-BCT particles exhibit some aggregation. It can be clearly seen in the TEM images that the BZT-BCT nanoparticles are completely covered by grafted PMMA. These results, in addition to the FT-IR and TGA data, clearly confirm that PMMA has been successfully grafted from the BZT-BCT surface.

Dielectric properties

Dielectric properties of all the samples were measured using an LCR meter (HP 4284A) at different frequencies ranging from 100 Hz to 1 MHz as shown in Fig. 5. Using the capacitance values, the dielectric constant for all the parallel plate dielectric capacitors was calculated at the same frequency range from 100 Hz to 1 MHz at room temperature using the following equation (2).

$$\epsilon = \frac{C*d}{\epsilon_0*A} \quad (2)$$

where ϵ is the dielectric constant of the material, C is the measured capacitance (pF) by the LCR meter, d is the thickness of the capacitor measured in centimeters (cm), ϵ_0 is the permittivity of the free space or vacuum (8.854 pF/m), and A is the surface area of the electrode of the capacitor calculated in cm^2 . The dielectric constant (ϵ) of a capacitor represents the ability of a material to store the charges during the dielectric polarization. In addition to high dielectric constant, low dielectric losses ($\tan \delta$) are mandatory for integral thin film capacitors, electrostriction systems for artificial muscles and electric stress control devices applications^{9b}. Dielectric loss is another important parameter in electrical capacitor applications. In general, capacitor performance is determined from the dielectric loss parameter; high dielectric loss will tend to dissipate a fraction of the stored energy in the form of heat and is detrimental to capacitor function.

In our earlier investigation we report high dielectric constant ($\epsilon \sim 400$ at 100Hz), low dielectric loss ($\tan \delta \sim 0.02$) properties at room temperature for BZT-BCT ceramic nanoparticles¹⁷. These ceramic nanoparticles have shown diffuse phase transition behavior for capacitor applications. Fig. 5 shows the frequency dependence of the dielectric constant and dielectric loss ($\tan \delta$) of the PMMA and polymer nanocomposites films investigated in the frequency range from 100 Hz to 1 MHz at room temperature. All the films have shown high dielectric constant at low frequency (100 Hz) and low dielectric constant at high frequency (1 MHz). This decrease in dielectric constant with frequency is attributed to the permanent dipole moments from the ferroelectric behavior of BZT-BCT ceramics that provide spontaneous polarization at room temperature thereby enhancing the dielectric constant values of the capacitor materials^{2b}.

The dielectric constant of the polymer grafted nanocomposites (F2) is significantly greater than that of F1, F3, F4, the dielectric constant values are $\epsilon \sim 6.5$ (F1), 56.55 (F2), 36 (F3), 32.34 (F4), respectively at 100 Hz. The dielectric constant of the core-shell structured PMMA graft BZT-BCT nanocomposite (F2) increased to 56.55, nearly 10 times that of the pure PMMA polymer films ($\epsilon \sim 6.5$). Significant dielectric constant increase could be explained by a number of important differences in the two films compared. Most obviously, the introduction of inorganic high dielectric constant ($\epsilon \sim 400$) of BZT-BCT as shown in Fig.S2¹⁷ filler particles are expected to improve the dielectric constant over PMMA alone. A second factor is that the covalent polymer-inorganic interface might allow large amounts of charge to accumulate between the two

distinct phases, generating interfacial polarization. In addition, the increased surface polarity caused by the introduction of polar initiating groups may play a role in improving the dielectric constant. This observation is consistent with previous reports which demonstrate that the surface functional groups at the nanoparticles/polymer matrix interface can have a profound effect on the electrical properties yielding improved dielectric properties for nanocomposites^{5, 6b, 13f, 22}.

Perhaps a more revealing comparison is that of film 3 against films 2 and 4. Film 3 only differs from film 2 by the addition of un-grafted PMMA (44.4% by weight). The significant drop in the dielectric constant suggests that substantial amounts of un-grafted PMMA only reduce the materials dielectric constant—consistent with the reduced dielectric constant of PMMA with respect to BZT-BCT. However, comparison of film 3 against film 4 provides additional insight. When comparing two films with the same amount of polymer (90%) and BZT-BCT (10%) content, the film with the surface grafted polymer performed measurably better, suggesting that the surface layer of polymer did play a role in improving the dielectric constant of these materials. Compared to the pure ungrafted BZT-BCT nanoparticles film F2 has shown significant increase in the breakdown strength. BDS for the pure nanoparticles ($\sim 0.073 \text{ MVcm}^{-1}$) was significantly enhanced for the grafted film (F2 $\sim 3 \text{ MVcm}^{-1}$) by almost 40 times. Even though, the dielectric constant for the film F2 (~ 56.55) was 4 times less than that of pure BZT-BCT nanoparticles (~ 400), the improvement in the breakdown and its quadratic dependence on the final energy density results in much higher energy storage values for the grafted nanoparticles film (F2) ($\sim 22.5 \text{ J/cm}^3$ at 3 MV/cm) than the pure BZT-BCT nanoparticles ($\sim 0.6 \text{ J/cm}^3$ at 0.073 MV/cm).

Fig. 5(b) also shows that the dielectric loss ($\tan \delta$) of F1 ~ 0.0188 , F2 ~ 0.02786 , F3 ~ 0.06250 and F4 ~ 0.08129 respectively at 100 Hz. Dielectric properties of pure BZT-BCT ceramics were displayed in Fig.S2. Over the whole frequency range measured the dielectric loss of the grafted and un-grafted nanocomposites is higher than of the pure PMMA. Although the relative importance of these parameters is not completely understood, it is clear the grafted BZT-BCT exhibit superior properties to the pure PMMA polymer itself. Meanwhile, the loss tangent of the nanocomposites remains quite low. The loss tangent for pure PMMA and for all other grafted and un-grafted polymer nanocomposite materials exhibited little variation in the frequency range

from 100 Hz to 1 MHz. As the frequency increases, dielectric loss for all the films decreased. The higher value of dielectric loss ($\tan \delta$) at a low frequency can be attributed to the space charge relaxation polarization mechanism. The dielectric loss of the nanocomposite was found to be slightly higher than the polymer matrix. From these results we can conclude that polymer grafted nanoparticles could be a promising material for fabricating dielectric materials for high dielectric constant films. We can see that the dielectric constant of these nanocomposites ($\epsilon \sim 56.55$) is much higher than that of PGMA grafted BaTiO₃ nanoparticles ($\epsilon \sim 15$) [15]; however dielectric constant for present pure PMMA polymer ($\epsilon \sim 6.5$) is similar ($\epsilon \sim 5$) to what has been previously reported by Liyuan et al.^{13d}. It is believed a significant portion of the increase in dielectric constant can be attributed to partial substitution of Ca²⁺ at the A-site and Zr⁴⁺ at the B site in typical ABO₃ type perovskite BaTiO₃. By suitable site engineering at both the Ba²⁺ and the Ti⁴⁺-sites in BaTiO₃, the dielectric properties can be optimized^{17, 24}.

Electric field dependent electrical energy density of pure PMMA (F1), polymer grafted BZT-BCT (F2) and partially blended film (F3) and un-grafted film (F4) were shown in Fig.6. Electrical energy storage of these dielectric capacitors was calculated using equation (1) due to linear polarization-electric field behavior as shown in Fig.S1 (supporting information). Leakage current behaviors of these films were also shown in Fig.S3 before the dielectric breakdown occurred. As the electric field increases electrical energy density of films increased drastically. It can be observed that the overall energy storage densities drastically increased (F2 ~ 22.5 J/cm³ @ 3MV/cm) for polymer-grafted films when compared to all other films (F1 ~ 10.3 J/cm³, F3 ~ 14.34 J/cm³, F4 ~ 12.88 J/cm³), however the maximum electric field (before the breakdown field occurred) of pure polymer is higher (~ 6 MV/cm) than that of nanocomposite films (~ 3 MV/cm). The enhanced energy density in the polymer-grafted nanoparticles mainly originates from the increased dielectric constant. Considering that, significant increase in dielectric constant of nanocomposites and comparable dielectric losses were due to the grafted polymer on the nanoparticles. Surface polymer grafting holds significant promise for further optimizing the dielectric properties of nanoparticles-based composite materials^{13d,23}.

Fig.7 shows the variation of ac electrical conductivity (σ_{ac}) for pure PMMA and polymer nanocomposites as a function of frequency (100 Hz-1 MHz). The ac conductivity was calculated

from dielectric properties using the relation $[\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan(\delta)]$. In most of the disordered materials, ac conductivity is directly proportional to the frequency. It is well known that, in large polaron hopping, the ac conductivity decreases with frequency whereas in small polaron hopping it increases with frequency. In the present case for all the samples, the plots for ac conductivity measurements are linear and increasing with respect to frequency, indicating the conduction is due to a small polaron hopping mechanism. Pure polymer capacitors have shown lower σ_{ac} (10^{-11} S/cm at 100 Hz) than that of all polymer-nanocomposites (10^{-10} S/cm at 100 Hz). The electrical conductivity of the samples, however exhibits strong dependence on the frequency. One can see that the introduction of BZT-BCT nanoparticles slightly increases the electrical conductivity of the nanocomposites (10^{-7} S/cm at 1 MHz). The overall electrical conductivity of pure polymer and polymer nanocomposites were low due low dielectric losses. The ac electrical conductivity of all the samples increases with the increase of frequency for all the samples and this is only slightly higher than that of pure PMMA over the whole frequency range measured, indicating the good insulating properties for all the samples^{13d}. The low electrical conductivity of nanocomposites is attributed to capping of BZT-BCT nanoparticles by insulating PMMA polymer shell and homogeneous dispersion in the polymer matrix, which prevented the electron conduction and when compared to pure PMMA, polymer grafted nanocomposites (BZT-BCT-g-PMMA) have a higher fraction of isotactic structure, which resulted in the lower leakage current and lower dielectric loss of these nanocomposites prepared by ATRP^{13d}.

Conclusions

BZT-BCT-PMMA nanocomposites with a PMMA coating were successfully prepared by SI-ATRP of MMA from the surface of BZT-BCT nanoparticles. A range of electronic measurements were utilized to compare the electric properties of pure PMMA film and BZT-BCT-PMMA nanocomposites films. AC conductivity measurements were in good agreement with universal power law. Low electrical conductivities on the order of 10^{-11} to 10^{-7} S/cm were observed in both the pure and nanocomposite films. Improved dielectric properties were observed for BZT-BCT-PMMA nanocomposite films, and are attributed to the even dispersion of nanoparticles within the polymer film, due to their improved compatibility upon grafting. Also, comparing films that were made from simple polymer/ceramic mixing with grafted BZT-BCT-PMMA/free polymer and pure BZT-BCT-PMMA nanocomposite reveals the importance of

covalent attachment between nanoparticle surface and polymer. Specifically, the nanocomposite films prepared from PMMA-grafted BZT-BCT nanoparticles exhibited high-energy storage densities ($\sim 22.5 \text{ J/cm}^3$ at 3 MV/cm) with respect to bulk PMMA ($\sim 10.39 \text{ J/cm}^3$ at 6 MV/cm). The significant improvement observed for polymer grafted BZT-BCT nanocomposites highlights the promise of grafted nanomaterials for optimizing future high-energy storage capacitor materials.

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Figure Captions

Scheme 1. Synthesis of BZT-BCT-PMMA core-shell nanoparticles by SI-ATRP of MMA from BZT-BCT nanoparticles.

Fig.1. X-ray diffraction patterns of BZT-BCT powder ceramics and the films (F1-F4)

Fig. 2. FTIR spectra of (a) as-prepared BZT-BCT, (b) BZT-BCT-CTCS, (c) BZT-BCT-PMMA, and (d) pure PMMA.

Fig.3. TGA curves of (a) as-prepared BZT-BCT, (b) BZT-BCT-CTCS, (c) PMMA-g-BZT-BCT, and (d) pure PMMA.

Fig.4. TEM images of (a) as-prepared BZT-BCT, (b) BZT-BCT-CTCS, (c) PMMA-g-BZT-BCT.

Fig.5 (a,b). Frequency dependent dielectric properties of (F1-F4) nanocomposite films at 100 Hz-1MHz.

Fig.6. Electric field dependent energy density properties of (F1-F4) polymer nanocomposite films.

Fig.7. Variation of A.C. conductivity with frequency of (F1-F4) polymer nanocomposite.

Fig.S1. Typical polarization-electric field (before dielectric breakdown occurred) loops for linear dielectric PMMA-g-BZT-BCT polymer nanocomposite films.

Fig.S2 (a, b) The temperature dependence of the dielectric constant and dielectric loss of $[(\text{BaZr}_{0.2}\text{Ti}_{0.8})\text{O}_3]_{1-x} - [(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3]_x$ ($x = 0.20$) - (BZT-BCT) ceramics.

Fig.S3 Electric field dependent leakage current behavior of (F1-F4) polymer and polymer nanocomposite.

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Scheme 1.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Graphic for Manuscript

Core-shell structured barium zirconium titanate-barium calcium titanate-poly(methyl methacrylate) [(Ba_{0.94}Ca_{0.06})(Zr_{0.16}Ti_{0.84})O₃-PMMA] nanocomposites were prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) of methyl methacrylate (MMA) from the surface of BZT-BCT nanoparticles. Polymer grafted BZT-BCT nanocomposite thick films (~10 μm) have shown an improved dielectric constant ($\epsilon \sim 56$), a high breakdown field strength (~3 MV/cm) and high-energy storage density ~22.5 J/cm³. The improved electrical properties of core-shell structured BZT-BCT-PMMA nanocomposites were attributed to improved nanoparticle dispersion and enhanced interfacial polarization due to the covalent linkage between polymer and nanoparticle interface. Mechanically stable and homogeneous composite films were obtained using the surface grafted BZT-BCT ceramic nanoparticles.