



# 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<sub>0.94</sub>Ca<sub>0.06</sub>)(Zr<sub>0.16</sub>Ti<sub>0.84</sub>)O<sub>3</sub>–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 ( $\epsilon \sim 56$ ), a high breakdown field strength (~3 MV/cm) and high-energy storage density ~22.5 J/cm<sup>3</sup>. 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.

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## 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<sub>3</sub> (BTO), and lead zirconium titanate, PbZrTiO<sub>3</sub>, (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 characteristics [1]. 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 requirements [2]. 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 ability [3]. However, most dielectric polymers possess relatively low dielectric constants ranging from 2 to 12 [4].

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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 permittivity [5]. 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 composite [5].

Accumulated energy storage density or volumetric energy density ( $E_d$ -in  $\text{J}/\text{cm}^3$ ) in linear dielectrics is determined by dielectric constant ( $\epsilon$ ), permittivity of free space ( $\epsilon_0$ ) and breakdown strength ( $E_b$ ).  $E_d$  has a linear relationship with dielectric constant ( $\epsilon$ ) 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 density [6]. 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 agglomeration [7]. Also, adding nano-sized  $\text{TiO}_2$  as an additive as opposed to micron-sized  $\text{TiO}_2$  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 composite [8]. 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 nanoparticles [9]. Surface hydroxylation of nanoparticles is another approach that was utilized to make nanoparticles disperse better in the polymer matrix [5]. Many other research efforts have also been reported for improving nanoparticles dispersion, such as surface modification of nanoparticles by organic molecules such as silanes [10], phosphonic acid [11], and ethylene diamine [12]; surface initiated in-situ polymerization

techniques [13]; 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 composites [15]. 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 capacitors [15,16].

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.

## 2. Experimental details

### 2.1. Materials

Methyl methacrylate (MMA, 99%, Aldrich) was purified by passing through basic alumina. Copper (I) bromide ( $\text{CuBr}$ , 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 technique [17]. The dielectric, ferroelectric and energy storage properties of BZT-BCT ceramic nanoparticles were reported elsewhere [17]. 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  $\text{BaTiO}_3$  nanoparticles (see supporting information for detailed grafting and thin film preparation) [13f].

### 2.2. 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  $\mu\text{m}$  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

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