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High-energy-density with polymer nanocomposites containing of $SrTiO_3$ nanofibers for capacitor application

Lingmin Yao[a], Zhongbin Pan[b], Jiwei Zhai[b,*], Guangzu Zhang[c], Zhiyu Liu[a], Yuhua Liu[a,*]

[a] School of Physics and Electronic Engineering, Guangzhou University, Guangzhou 510006, China
[b] School of Materials Science & Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, China
[c] School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

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ABSTRACT

Inorganic/polymer nanocomposite films have attracted pronounced attention for electric energy storage applications since their high power energy density and fast charge-discharge ability. In this work, the flexible nanocomposite films composed by the paraelectric $SrTiO_3$ nanofibers (ST NFs) and poly(vinylidene fluoride) (PVDF) were prepared by a solution cast method. The ST NFs, synthesized by an electrospinning method, were coated with a dense and robust dopamine layer which could effectively improve the filler-matrix distributional homogeneity and compatibility. The composite film with an optimized filler content illustrates a high discharge energy density of 9.12 J/cm^3 at 360 MV/m, which is about 625% over the biaxially oriented polypropylenes (BOPP) (1.2 J/cm^3 at 640 MV/m). Moreover, the composite film shows a superior power density of 2.31 MW/cm^3 and ultra-fast discharge speed of 178 ns. Therefore, the present approach might be extended to the fabrication of similar polymeric nanocomposites for high-performance capacitor energy storage devices.

1. Introduction

The fast-growing energy market in portable electronics, pulsed power system, vapor/liquid sensors and electric vehicles demands high property dielectric materials featuring low-cost, light weight, high energy density, and high temperature capability [1–6]. Generally, the energy density (U_e) in a dielectric capacitor is determined simultaneously by the applied electric field (E) and the electric displacement (D) as $U_e = \int_{D_{\max}}^{0} E dD$ [7]. For linear dielectrics, the U_e could be described as $U_e = \frac{1}{2}\varepsilon_r \varepsilon_0 E_b^2$, where ε_r is the relative dielectric permittivity, ε_0 (8.85×10^{-12} F m^{-1}) is the vacuum constant, and E_b is the breakdown strength [8]. In order to increase the energy density of dielectric capacitors, one method is to increase either the dielectric constant or breakdown strength. For the first glance, it seems that increasing breakdown strength can be more attractive because the power density enhances with the square of breakdown strength. In this regard, ceramic/polymer nanocomposite films, combining the best aspects of ceramic (high dielectric constant) and polymer matrix (high breakdown strength), have become a hot research topic in the field of dielectric materials. Because the ceramic/polymer nanocomposite have the potential to simultaneously optimize the two factors (E_b and ε_r) that determine the high energy density [9–19].

Traditionally, ferroelectric ceramics, including $BaTiO_3$ [20–22], $BaSrTiO_3$ [23], $PbZrTiO_3$ [24], $NaNbO_3$ [25], $0.5(Ba_{0.7}Ca_{0.3})TiO_3$–$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ [26,27], and $CaCu_3Ti_4O_{12}$ [28,29], have been preferred choices as the fillers in polymer matrix since their high dielectric constant. However, the discharge efficiency would decrease when the ferroelectric ceramics were incorporated into the polymer matrix owing to the essential large remnant polarization in ferroelectric ceramics. In addition, the large dielectric constant contrast between high-dielectric-constant fillers and low-dielectric-constant polymeric matrix could cause serious mismatch, which would further reduce the dielectric breakdown strength of nanocomposite films [30]. $SrTiO_3$ is considered to be an excellent lead free paraelectric ceramic with a high relative permittivity of approximately 300 at 1 kHz, which has attracted significant interest because of its potential to replace lead based ceramic materials [31]. Therefore, using paraelectric ceramic fillers in the nanocomposite films, such as $SrTiO_3$, would provide not only relatively high dielectric constant but lower remnant polarization [31]. The low remnant polarization would result in lower energy loss, which is beneficial for improving the energy density of the nanocomposite films.

In addition, the microstructural morphology and concentration of the filler play dominant roles in the energy storage density of polymer nanocomposites [32–34]. As reported, compared with zero-dimensional (0D) fillers, one dimensional (1D) filler with high-aspect-ratio are more effective in enhancing the dielectric performance and energy density of polymer nanocomposites under the similar condition [7,35–37]. Small

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* Corresponding authors.
E-mail addresses: apzhai@tongji.edu.cn (J. Zhai), liuyuhua@gzhu.edu.cn (Y. Liu).

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specific surface of large-aspect-ratio fillers could further reduce surface energy and decrease nanofiller agglomeration in the polymer matrix. Recently, we have indicated that nanocomposite loading with 4 vol% 1D $BaTiO_3$ nanofibers exhibits larger dielectric constant (14.69 vs. 11.03 at 1 kHz), higher breakdown strength (300 vs. 370 MV/m) and enhanced energy density (8.78 vs. 4.86 J/cm^3) as compared with the 0D $BaTiO_3$ nanoparticles under the same conditions [38].

Generally, the enormous specific surface area of nanofillers would lead to aggregation and inhomogeneity distribution of fillers in the polymeric matrix, which would further cause serious deterioration in dielectric properties [6,39–42]. In order to improve filler's dispersion, many studies have been carried out by the incorporation of functional groups onto the surface of nanofillers through chemical modification, thus improving the interaction between fillers and polymer matrix, and preventing their agglomeration. For example, Jiang et al. [43] prepared core-shell structured hyperbranched aromatic polyamide@$BaTiO_3$ (HBP@BT) as fillers in PVDF matrix through atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) polymerization,. The dielectric constant at 1 kHz was greatly improved after loading with 40 vol% HBP@BT (206.3 vs. 1485.5).

In the present study, novel films were prepared by employing poly (vinylidene fluoride) (PVDF) blends as the polymer matrix and high-aspect-ratio paraelectric $SrTiO_3$ nanofibers (ST NFs) as fillers to form nanocomposites through solution cast method. The large-aspect-ratio 1D ST NFs were prepared via electrospinning method. The dopamine was coated onto the surface of ST NFs to improve the dispersion and compatibility of the nanofillers in the polymer matrix. In addition, the dopamine layer acting as shell layer confines the movement of the charge carriers in the interface filler/matrixes and thereby decreasing the dielectric loss. As a result, The composite films with an optimized filler content illustrate a high discharge energy density of 9.12 J/cm^3 at 360 MV/m, which is about 625% over the biaxially oriented polypropylenes (BOPP) (1.2 J/cm^3 at the field of 640 MV/m). Moreover, the composite films show a superior power density of 2.31 MW/cm^3 and ultra-fast discharge speed of 178 ns.

2. Experimental

2.1. Materials

All chemicals of analytic grade except the Poly(vinylidene fluoride) (PVDF, Arkema, Kynars 301F) were supplied by Shanghai Aladdin Industrial Inc.

2.2. Synthesis of $SrTiO_3$ nanofibers

The $SrTiO_3$ nanofibers (ST NFs) were synthesized via electrospinning technique. First, $Sr(COOH)_2$ (2.19 g) was dissolved in CH_3CH_2COOH (10 ml) and stirred at 50 °C for 1 h to form a homogeneous precursor solution A (Sol A). Second, the $C_{16}H_{36}O_4Ti$ (2.92 g) was dissolved in acetylacetone (2 g) and stirred to form a stable precursor solution B (Sol B). Third, the Sol B was added into Sol A and stirred to form a stable precursor solution C (Sol C). The viscosity of solution C was adjusted by the addition of PVP. The solution C was then moved to a syringe for electrospinning at 1.7 $kV\,cm^{-1}$. The co-electrospinning nanofibers were air-calcinated at 700 °C for 3 h to form ST NFs. The composition and morphology of ST NFs were characterized by HRTEM and FESEM.

2.3. Modification of ST NFs

To effectively improve the filler-matrix compatibility, dopamine was employed as a surface modifier. The ST NFs were dispersed in 0.02 $mol\,L^{-1}$ dopamine hydrochloride solutions under stirring at 60 °C for 12 h, followed by drying at 80 °C for 10 h and named as dopamine-coated ST NFs (ST@PDA NFs). The dense and robust surface layers of dopamine were observed by HRTEM and further evidenced by FT-IR.

2.4. Fabrication of nanocomposite films

The nanocomposite films were prepared as follows. The ST@PDA NFs and PVDF were proportionally dissolved into DMF by stirring at 70 °C for 24 h, forming a stable suspension D. The suspension D was cast onto the ITO substrate to form nanocomposite films, which were vacuum-dried at 45 °C for 10 h to volatilize the solvent and eliminate structural defects. Pristine PVDF films were treated in the same way for comparison. The final nanocomposite films were ≈10 μm thick and their morphology were characterized by FESEM.

2.5. Measurement of dielectric properties

The aluminum electrodes (60 nm in thickness and 2 mm in diameter) were sputtered on the nanocomposite films for electrical measurements. Their dielectric constant and dielectric loss were measured by an E4980A LCR meter in the frequency range 10^2 Hz to 10^6 Hz with 1000 mV at ambient temperature (various). The leakage current density was characterized by a Keithley 2400 source meter (Keithley Instruments, Inc.). The D-E hysteresis of the nanocomposite films were characterized by a Premier II ferroelectric test system at 10 Hz.

3. Results and discussion

The 1D architecture ST NFs could be easily obtained after 3 h of heating at 700 °C. The typical SEM images of ST NFs are exhibited in Fig. 1a. Clearly, the ST NFs have high aspect ratio with the diameter of 150–250 nm and length a few tens of micrometers, as indicated by the FESEM in Fig. 1a. The XRD patterns of BT NTs are presented in Fig. 1b. Clearly, the diffraction peaks at $2\theta = 22.81°$, 32.41°, 39.97°, 46.48°, 52.38°, 57.82°, 67.80°, and 77.19°can be indexed to the (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), and (3 1 0) reflections of perovskite $SrTiO_3$ (PDF 35-0734). The microstructures and composition of the complex ST NFs were further characterized by HRTEM. The sample clearly shows large aspect ratio (Fig. 1c). The d spaces estimated from the lattice fringe are 2.755 ± 0.005 nm (Fig. 1d), which correspond to the [1 1 0] crystal direction of the ST NFs. It is indicated that the ST NFs obtained by electrospinning method have a perovskite structure, which is consistent with the XRD data.

The sufficient dispersion and compatibility between the fillers and matrix is one key factor that improves the dielectric constant and breakdown strength of dielectric capacitors. The filler/matrix compatibility and dispersion of the ST NFs were effectively improved by modifying with dopamine. Clearly, the homogeneous amorphous about 10 nm polymer coating layer atop the ST NFs is formed through the dopamine oxidative self-polymerization (Fig. 2a). This amorphous coating layer was further characterized by FT-IR. Compared with the unmodified ST NFs samples, the FT-IR spectra in Fig. 2b shows additional absorbance signals at 1258 cm^{-1} (—C—N stretching vibration), 1499 cm^{-1} (aromatic —C—C stretching vibration), 1630 cm^{-1} (—NH bending vibration) owing to dopamine [44,45], and 3100–3700 cm^{-1} (—NH and/or —OH stretching vibrations). The experimental results indicate that the ST NFs surface has been successfully coated with dopamine. The nanocomposite films have been were prepared by a solution casting method. The top-view images and cross-sectional view of nanocomposites filled with 5 vol% ST-PDA NFs are shown in Fig. 2(c) and (d). Clearly, the ST NFs are well dispersed into the polymer matrix with the help of the dense polymer surface layer of dopamine. The SEM images show uniformity dispersion and good interfacial adhesion of ST-PDA NFs inside the PVDF matrix, which is the key factor to improve the dielectric constant and breakdown strength of the nanocomposites films.

Frequency-dependent dielectric constant and dielectric loss of