



Fabrication and characterization of free-standing, flexible and translucent BaTiO₃-P(VDF-CTFE) nanocomposite films

Xu Lu^{a, b, *}, Yang Tong^b, Z.-Y. Cheng^{b, **}

^a Laboratory of Functional Films, School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, China

^b Materials Research and Education Center, Auburn University, Auburn, AL, 36849, USA



ARTICLE INFO

Article history:

Received 9 May 2018

Received in revised form

1 August 2018

Accepted 19 August 2018

Available online 20 August 2018

Keywords:

Ceramic-polymer nanocomposite

Dielectric

Energy-storage

ABSTRACT

Free-standing and translucent nanocomposite films with good flexibility were fabricated using a spin-coating process. BaTiO₃ nanoparticles with an average size of about 50 nm and P(VDF-CTFE) 91/9 mol.% copolymer were used as ceramic fillers and polymer matrix, respectively. Dense and uniform microstructure was obtained due to the good compatibility and homogeneous distribution of BaTiO₃ nanoparticles in P(VDF-CTFE) matrix. It was experimentally found that the dielectric constant increased but the breakdown strength decreased with increasing volume fraction of BaTiO₃. A dielectric constant of about 53 was obtained in the nanocomposite film with 40 vol.% of BaTiO₃, which was about 4.4 times higher than that of the pure P(VDF-CTFE) film. A discharged energy-storage density of 4.9 J/cm³ was obtained in the nanocomposite film with 35 vol.% of BaTiO₃ under 2000 kV/cm, which was about 2 times higher than that of the pure P(VDF-CTFE) film under the same electric field.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, composite approaches have been widely investigated to combine the high dielectric constant (ϵ_r) of ceramics and the high breakdown strength (E_b) of glasses/polymers to develop advanced dielectric materials for energy-storage applications [1–8]. Ceramic-glass composites can be sintered from either a random mixture of ceramic and glass powders or glass-coated ceramic particles, which can be applied in a wide working temperature range [9–12]. On the other side, ceramic-polymer 0–3 composites can be easily fabricated by dispersing ceramic fillers into polymer matrices, which are flexible and can be processed at room temperature [13–15].

From an application point of view, flexible composite films with high ϵ_r and high E_b are highly desirable for the fabrication of energy-storage devices. Therefore, a lot of researches have been focused on the ceramic-polymer composites. Polymers with both high E_b and high ϵ_r , such as PVDF based polymers [16–20], etc., can be used as matrices. Ceramic particles with high ϵ_r , such as BaTiO₃

(BT) [21–23], (Ba,Sr)TiO₃ (BST) [24–27], Pb(Zr,Ti)O₃ (PZT) [28,29], CaCu₃Ti₄O₁₂ (CCTO) [30,31], etc., have been used as fillers. The ϵ_r of a ceramic-polymer composite is determined by the composition and the dielectric constants of its constituents. The E_b of a ceramic-polymer composite is not only determined by the composition and the breakdown strengths of its constituents but also significantly affected by the fabrication processes, which affect the distribution and compatibility between ceramic fillers and polymer matrices [32]. Substantial research efforts have been undertaken to obtain homogeneous distribution and good compatibility between ceramic fillers and polymer matrices. Hot pressing process was utilized to improve the distribution condition and uniformity of ceramic-polymer composites fabricated using solution-casting process by pressing a stack of composite films into one layer [14,25,30,33,34]. Surface treating methods were widely used to improve the compatibility between ceramic fillers and polymer matrices [35–39]. Although the hot pressing and surface treating can successfully improve the properties of ceramic-polymer composites, the fabrication processes are much more complex [38]. Simple and effective fabrication processes are demanded for the investigations of ceramic-polymer composites.

In this work, a simple spin-coating process was used to fabricate free-standing films of ceramic-polymer nanocomposites. The ceramic nanoparticles-polymer suspensions used in the spin-coating process were designed to be much thicker than those

* Corresponding author. Laboratory of Functional Films, School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, China.

** Corresponding author.

E-mail addresses: lux@xaut.edu.cn (X. Lu), chengzh@eng.auburn.edu (Z.-Y. Cheng).

used in the solution-casting process, which resulted in the suspensions with a great stability. In addition, due to the thick suspensions with less solvent, the solidification of the nanocomposite films in the spin-coating process was much faster than that in the solution-casting process. As results, the non-uniformity caused by the sedimentation of ceramic fillers during the solidification could be significantly eliminated so that homogeneous distribution and good compatibility between ceramic fillers and polymer matrix could be obtained. In the experiments, commercially available BT nanoparticles with an average size of about 50 nm were used as ceramic fillers due to the high dielectric constant. P(VDF-CTFE) 91/9 mol.% copolymer (VC₉₁) was used as polymer matrix due to the weak temperature dependence of dielectric constant above its glass transition temperature and the good flexibility related to its low crystallinity. Free-standing, flexible and translucent BT-VC₉₁ nanocomposite films were successfully fabricated using the spin-coating process, and the dielectric properties and energy-storage performances were systematically investigated.

2. Experiments

BT-VC₉₁ nanocomposite films were fabricated using commercially available materials. BT nanoparticles with an average size of about 50 nm, VC₉₁ powder, and dimethylformamide (DMF) were purchased from nGimat, Solvay, and Fisher Scientific, respectively. All the materials were used as received. The volume fractions of BT nanoparticles in the resultant nanocomposite films were chosen as x vol.% ($x = 0, 5, 10, 15, 20, 25, 30, 35$ and 40). For the fabrication of each nanocomposite film with a certain volume fraction of BT, the VC₉₁ powder was 1.5 g, and the mass of BT nanoparticles was calculated from the composition. In the calculations, the densities of BT nanoparticles and VC₉₁ powder were assumed as that of the bulk materials, which were 6.02 g/cm³ and 1.75 g/cm³, respectively. The BT-VC₉₁ nanocomposite film with x vol.% of BT was abbreviated as x BT-VC₉₁ in the following discussions.

The detailed fabrication process of the BT-VC₉₁ nanocomposite films are given below. Firstly, BT nanoparticles were dispersed in 10 mL DMF by magnetic stirring for one hour and by ultrasonication for one hour. Then, 1.5 g VC₉₁ powder was added in and the mixture was magnetic stirred until all the VC₉₁ powder dissolved. After that, the mixture of BT-VC₉₁-DMF was fully dispersed by ultrasonication and magnetic stirring alternately for 10 h to obtain a stable and uniform BT-VC₉₁-DMF suspension. A simple spin-coater was used to make films on glass substrates, and the program was set as 300 rpm for 30 s. About 1.5 mL of the BT-VC₉₁-DMF suspension was dropped on a glass substrate and the spin-coater was run subsequently. The coated layer with glass substrate was put in an oven at 80 °C for one hour to evaporate the solvent. Finally, the solidified film was peeled off from the glass substrate in distilled water, and the obtained free-standing film was then annealed at 140 °C in air for 24 h. After annealing, the thicknesses of the BT-VC₉₁ nanocomposite films varied with the volume fraction of BT, from about 5 μm for the pure VC₉₁ film to about 11 μm for the 40BT-VC₉₁ film. The annealed films were used as BT-VC₉₁ nanocomposite films in the following characterizations.

The morphology and microstructure of the BT-VC₉₁ nanocomposite films were examined by using a field emission scanning electron microscope (FESEM, JEOL JSM-7000F). X-ray diffraction (XRD, PANalytical) was adopted to identify the phase composition of the BT-VC₉₁ nanocomposite films over a 2θ range from 10° to 60°. For electrical measurements, gold electrodes with a diameter of 3 mm were sputtered on both sides of the BT-VC₉₁ nanocomposite films by using a gold coater (PELCO SC-6). The capacitance and dielectric loss tangent ($\tan\delta$) were measured using an Agilent 4294A precision impedance analyzer in the frequency range from 100 Hz to 1 MHz and in the temperature range from -60 °C to 120 °C by placing the samples in an Espec ECT-2 temperature chamber. The ϵ_r was converted from the capacitance using the parallel-plate mode with known area and thickness. The E_b was measured using a 10 kV H.V. Supply/Amplifier. The polarization-

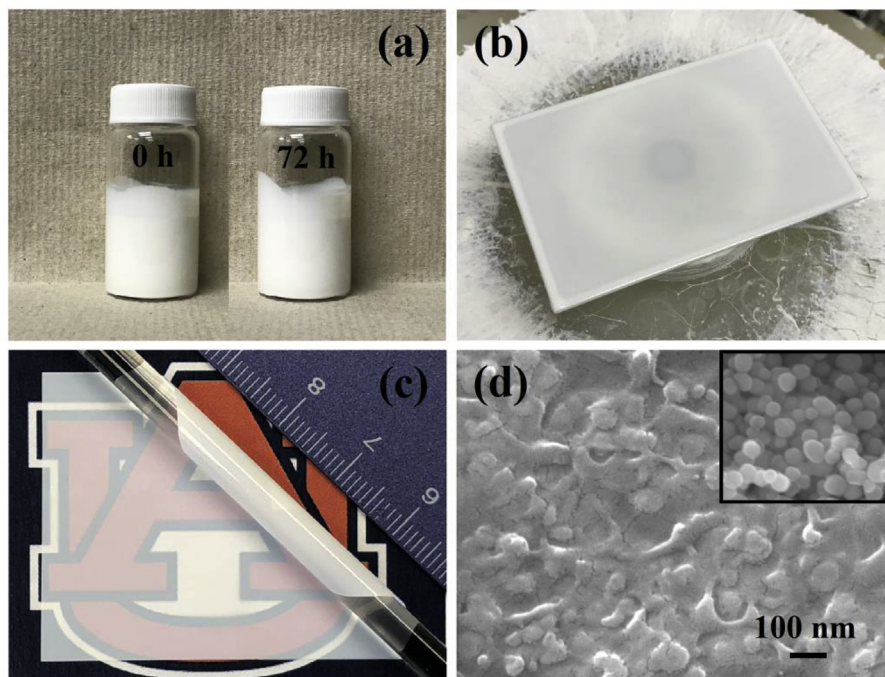


Fig. 1. (a) Suspension used for the fabrication of the 20BT-VC₉₁ nanocomposite film; (b) the spin-coating process used in this work; (c) 40BT-VC₉₁ nanocomposite film twisted around a thin glass bar; (d) SEM images of the BT nanoparticles and a typical cross section for the 20BT-VC₉₁ nanocomposite film.

Download English Version:

<https://daneshyari.com/en/article/8943299>

Download Persian Version:

<https://daneshyari.com/article/8943299>

[Daneshyari.com](https://daneshyari.com)