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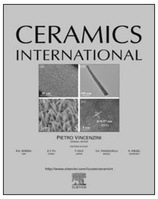

Mechanism of enhanced dielectric performance in $Ba(Fe_{0.5}Ta_{0.5})O_3$/poly(vinylidene fluoride) nanocomposites

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ABSTRACT

An organic-inorganic 0–3 nanocomposites, in which nanoparticles (0-dimensional) are embedded in a 3-dimensionally connected polymer matrix, rapidly emerged for a number of advanced engineering applications. The nanocomposites with enhanced dielectric performance is realized by employing $Ba(Fe_{0.5}Ta_{0.5})O_3$ (BFT) with giant dielectric constant (ε') as a ceramic filler and poly(vinylidene fluoride) (PVDF) as a polymer matrix. The dense nanocomposites use the hot-press process, which can eliminate the porosity. Experimental data shows that dielectric constant of the nanocomposites with 60 vol% of BFT can reach 97 at 100 Hz, which is attributed to the individual dielectric constant of BFT and PVDF, and enhanced interfacial polarization. Meanwhile, the soft percolation regime is found at the volume filling fractions of BFT between 0.2 and 0.3, which also plays an important role in enhanced dielectric constant. Different theoretical models are applied to predict the dielectric constants of the nanocomposites. Furthermore, the introduction of BFT nanoparticles improves the temperature stability of dielectric constant in the temperature range from 20 °C to 120 °C.

1. Introduction

By integrating two or more materials with complementary properties, nanocomposites offer the potential to have performance far beyond those of the constituent materials [1]. Polymer based dielectric nanocomposites have brought about considerable attention for applications in energy harvesting/storage devices, integrated capacitors, actuators, and power cable termination due to their inherent advantages of mechanical flexibility, facile processability and economical efficiency [2]. The most common and promising strategy to obtain polymer based nanocomposites with enhanced dielectric constant is adding ceramic particles with high dielectric constant into the polymer matrices, which capitalizes upon the idea that it combines colossal permittivity of ceramic particles and good dielectric strength of polymers [3].

Choice of suitable polymer is important for a high dielectric constant nanocomposite. Poly(vinylidene fiuoride) (PVDF) has received much attention due to its higher dielectric constant. In recent years, it has become a hot issue, which is obtaining high dielectric constant in PVDF based nanocomposites via introducing ceramic nanoparticles with high dielectric constant [4]. In general, ferroelectric or relaxor ferroelectric ceramics, such as $BaTiO_3$ (BT) [5,6], $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) [7] and $Pb(Zr,Ti)O_3$ (PZT) [8] have been the most commonly used fillers in polymer nanocomposites. However, the value of dielectric constant of the nanocomposites (usually $\varepsilon' < 50$) is limited by the dielectric constant of ceramic fillers. For example, Yu et al. [9] have reported that the dielectric constant of a ferroelectric polymer poly(vinylidene fuoride) at 1 kHz increased from 10 to 40 after blending with 50 vol% of surface-modified barium titanate (BT) nanoparticles ($\varepsilon' < 2 \times 10^3$). Furthermore, the temperature stability of dielectric constant is important for theirs widely application. Thus, it is necessary to develop a new composition of ceramic/polymer nanocomposites. Meanwhile, $Ba(Fe_{0.5}Ta_{0.5})O_3$ (BFT) ceramics generally exhibit a giant dielectric constant ($\varepsilon' > 10^4$), broad temperature and frequency interval [10]. It is mean that there is no detected phase transition when the ceramics are cooled through a critical temperature [11]. Compared with $CaCu_3Ti_4O_{12}$, BFT also has lots of advantages, such as: low calcination temperature, briefer calcining time and smaller particles size. The remarkable dielectric properties of BFT ceramics make BFT powders be an excellent candidate of the filler in high dielectric constant ceramic-polymer nanocomposites.

In this work, the novel nanocomposites were prepared by embedding the BFT nanoparticles into PVDF matrix. The crystal structure, microstructure and dielectric properties of the BFN/PVDF nanocomposites were discussed in detail. Various theoretical models like Maxwelle-Garnett, Jayasunderee-Smith and effective medium theory (EMT) were employed to research the dielectric behaviors of these biphasic nanocomposites. Compared with our previous work, the

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composite with 60 vol% of BFT exhibited the higher dielectric constant and temperature stability [11]. Furthermore, we hoped to open the doors to reveal the mechanism of enhanced dielectric performance in such ceramic-polymer nanocomposites.

2. Material and methods

The iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), barium nitrate ($Ba(NO_3)_2$) and oxalic acid dehydrate ($(COOH)_2 \cdot 2H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tantalum chloride ($TaCl_5$) was supplied by Alfa Aesar Co., Ltd. Ammonium hydroxide (25.0–28.0%) was obtained from Xilong Chemical Reagent Co., Ltd. The poly(vinylidene fluoride) (PVDF), molecular weight of MW 534,000 supplied by Sigma-Aldrich Co., LLC.

The nanometer scale $Ba(Fe_{0.5}Ta_{0.5})O_3$ powders were synthesized by oxalate coprecipitation method which could obtain smaller particles size than the conventional solid-state reaction. Ferric nitrate, barium nitrate and oxalic acid were dissolved in distilled water and Tantalum chloride was dissolved in ethanol. All solutions were thoroughly mixed in ambient conditions using magnetic stirrer. Then some ammonia was dripped into the oxalic acid solution slowly until the pH value was adjusted to 10. The precursor was kept stirring for 3 h for the complete reaction. After drying, the calcination of the precursor powder is made at 1000 °C for 2 h to obtain the nanometer scale BFT powders. The nanocomposites were prepared using physical mixing method. The $Ba(Fe_{0.5}Ta_{0.5})O_3$ powders and PVDF were weighed accurately and mixed by vibro-milling for 1 h. Then the mixture was drying for 24 h at 80 °C. Finally, the mixture of BFT fillers and PVDF at the volumetric fraction of 0–60% was molded by hot-pressing at ~ 160 °C, 78 MPa for 30 min.

X-ray diffraction (XRD) patterns of all samples were collected at room temperature on a Rigaku Corporation X-ray diffractometer (D/max-2200PC). The fractured surface morphology of the samples was examined by scanning electron microscopy (SEM, S-4800). For SEM imaging, nanocomposites were initially frozen in liquid nitrogen, then fractured and sputter-coated with a homogeneous gold layer. The dielectric properties of the nanocomposites were measured using an impedance analyzer (Agilent-E4980A) in the frequency range of 20 Hz–2 MHz.

3. Results and discussion

The X-ray diffraction patterns of BFT powder, PVDF powder, hot-press PVDF disk, and the nanocomposites with different volume fractions of BFT are illustrated in Fig. 1. Compared to the remarkable diffraction peaks of perovskite type BFT, XRD patterns of PVDF before and after hot-press process exhibit a typical characteristic hump of semi-crystalline structure. The peaks of PVDF powders at 2θ = 18.30° (100), 19.86° (021) and 26.6° (100) are assigned to the α-phase. However, part of α-phase transforms to β-phase after hot-press process, which is proved by the existence of the peaks of (110) and (200) (2θ = 21.04°) and the peaks of (021) and (101) (2θ = 36.64°). As is well known, β-phase of the PVDF has highest dipole moment of 2.10 D in perpendicular to chain length [12]. The partial formation of β-phase is beneficial for the enhancement of the dielectric constant of the nanocomposites. The peaks intensity for β-phase of PVDF has decreased as compared to that of BFT peaks in nanocomposites as the volume fractions of BFT increased in PVDF, which can be ascribed to the shielding effect for high intensity of diffraction peaks in BFT.

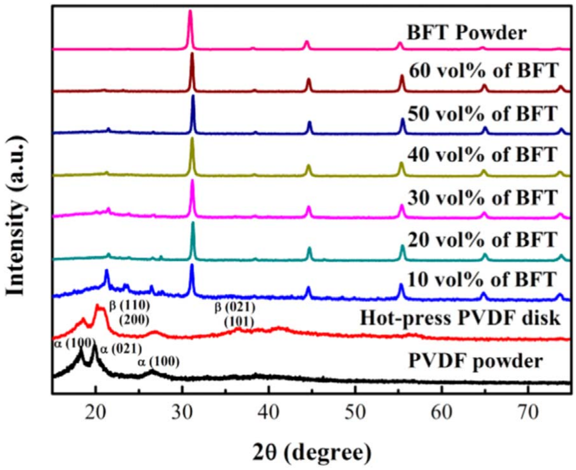

Fig. 1. XRD patterns of BFT powder, pure PVDF powder, hot-press PVDF disk, and the nanocomposites with different volume fractions of BFT.

The morphology and dispersion of the particles in the BFT/PVDF nanocomposites are observed by scanning electron microscopy (SEM) and the results are shown in Fig. 2. As shown in Fig. 2(a), the PVDF disk forms a continuous phase. Fig. 2(b)–(g) show the fractured cross section morphologies of nanocomposites filled with 10, 20, 30, 40, 50 and 60 vol% of BFT powders, respectively. It is observed that the BFT powders with the particle sizes of 80–100 nm are homogeneously dispersed on the PVDF at low filler content of BFT powder. With the content of BFT increasing, fillers of particles grow denser and aggregated, which is unavoidable at high volume fractions of fillers in nanocomposites.

The dielectric properties of the PVDF nanocomposites are studied by a dielectric spectroscopy from 20 Hz to 2 MHz at room temperature. Fig. 3 shows the frequency dependence of dielectric constant and dielectric loss tangent of the PVDF nanocomposites. From Fig. 3(a), it can be discovered that the dielectric constant increases with the increase of BFT contents and sharply decreases with the increase of frequency. As the concentration of BFT fillers is increased to 10, 20, 30, 40, 50 and 60 vol%, the values of dielectric constant at 100 Hz increase to 20.0, 30.3, 57.9, 65.8, 75.0, 97.4, respectively. For the nanocomposites with 60 vol% of BFT, the dielectric constant at 100 Hz is nine times higher than that of PVDF disk. The increase in dielectric constant of the nanocomposites is partially originated from the introduction of giant dielectric constant BFT particles, which result in average electric field enhancement in the polymer matrix [13]. Furthermore, at low frequency of 20 Hz ~ 1 kHz, the dielectric constant with different amounts of BFT in nanocomposites decreases with the frequency increasing, which is due to the interfacial polarization. The motion of space charges in the interface zone under the applied electric field induces significant polarization, thus producing high dielectric constant [14]. When the interfacial polarization cannot keep up with the change of the frequency, the dielectric constant originated from the interfacial polarization decreases with the rise of the frequency. Interestingly, when the loadings of BFT particles are from 20 vol% to 30 vol%, the dielectric constant increases greatly with the increasing BFT contents. It can be explained that there is an insulator-conductor transition due to the formation of continuous networks in the polymer nanocomposites. Motions of the mobile space charges within the percolation paths through tunneling then give rise to much stronger space charge polarization [15]. Difference with the normal percolation regime in carbon and metal filler/polymer composites, which forms conductive paths by the conductor themselves, soft percolation regime forms conductive paths by space charges among interfaces. When the frequency is increasing, the varying trend of the dielectric loss tangent is similar to the dielectric constant (shown in Fig. 3(b)). The difference is that the dielectric loss tangent increases with frequency over 1 MHz. It is related to the micro-Brownian cooperative motions of the main chain backbone and dielectric manifestation of the glass transition of PVDF [16].

The dielectric constant of a polymer nanocomposite depends on the individual dielectric constant of fillers and polymer matrix along with different filler loadings and interactions among them [17]. To clarify