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Enhancement of dielectric and electrical properties in BFN/Ni/PVDF three-phase composites

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A B S T R A C T

To develop dielectric materials with high dielectric constant and low dielectric loss, a novel three-phase composite was prepared by embedding the nano-sized $Ba(Fe_{0.5}Nb_{0.5})O_3$ (BFN) crystallites and Ni crystallites into poly(vinylidene fluoride) (PVDF) matrix. The structure, dielectric and electrical properties of the composites were investigated. The superiority of this method is that, when compared with the two-phase Ni/PVDF composites, three-phase composites not only show significantly increased dielectric constants but also have lower dielectric loss. Our results show that a high dielectric constant of 475 and a relatively low loss of 0.61 were achieved at 100 Hz with 25 vol.% Ni and 50 vol.% BFN, respectively. The enhancement of dielectric constant of polymer based composites can be interpreted by the mini-capacitor principle and the interfacial polarization. The relatively low dielectric loss could be attributed to the isolation effect of BFN fillers. These composites with high dielectric constant and low dielectric loss are found to be potentially useful for embedded capacitor applications.

1. Introduction

With the tendency of miniaturization and multifunction of the electronic systems, dielectric materials with high dielectric constant, low dielectric loss and excellent processing performance are highly desired and essential for practical applications [1]. Polymer materials have merits of low-temperature processing, high electric breakdown strength and excellent flexibility [2]. However, the low value of dielectric constant of polymer materials (2–5) impedes their applications. Hence, polymer based composites with the advantages of good mechanical and dielectric performance have drawn considerable attentions in recent years.

The traditional two-phase polymer based composites consist of ceramic/polymer composites and conductor/polymer composites. On the one hand, ceramic/polymer composites capitalize upon the idea that the combination of colossal constant of ceramic crystallites with good dielectric strength of polymers may result in polymer based flexible composites with enhanced dielectric properties [3]. $BaTiO_3$ [4,5], $Pb(Zr, Ti)O_3$ [6,7], $BaSrTiO_3$ [8,9], $K_{0.5}Na_{0.5}NbO_3$ [10,11] and $CaCu_3Ti_4O_{12}$ [12,13] ceramics gain much attentions because of the significant characteristic of dielectric constant. However, due to the composition and structure limitation of this kind of composites, the dielectric constant of ceramic/polymer two-phase composites is still not high enough (below 100) to satisfy the demands of practical applications [14]. On the other hand, the introduction of conductive fillers into polymer matrices is another attractive approach to obtain high constant polymer based composites. Various conductive fillers, such as silver (Ag), aluminum (Al), nickel (Ni), and carbon nanotube (CNT) [15–18], have been used to prepare the polymer conductive filler composites. The value of dielectric constant of conductor/polymer composites increases by several orders of magnitude when the filler content is in the neighborhood of percolation threshold. And the drastic enhancement of dielectric constant of conductor/polymer two-phase composites can be interpreted by percolation theory [19]. However, the occurrence of insulator-conductor transition in the percolative composites leads to a high dielectric loss on account of the relatively large leakage current. Meanwhile, the dielectric constant becomes very sensitive to the composition variation when the volume fraction of conductive fillers approaches to percolation threshold [20]. These severe drawbacks of conductor/polymer two-phase composites weaken their dielectric performance and limit the use of conductive fillers polymer based composites in actual devices [4].

To overcome these drawbacks, a large amount of efforts have been devoted to develop three-phase polymer based composites

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incorporating conductive fillers and ceramic fillers, such as: Ni/$BaTiO_3$/PVDF, Ag/$BaTiO_3$/epoxy and graphene/$BaTiO_3$/PVDF [21–23]. As the high dielectric constant in the conductor/polymer composites, the introduction of third phase aims at increasing the low dielectric constant and decreasing the high dielectric loss in the neighborhood of percolation threshold. The enhancement of dielectric constant is that the incorporation of ceramic results in enhanced interfacial polarization effect. The decline of dielectric loss is that the introduction of ceramic with poor conductive property prevents the formation of conductive networks.

The key issue of obtaining the polymer based composites with excellent dielectric performance is to choose appropriate fillers and polymer matrices. The most widely used polymer matrices are polyimide (PI), epoxy, polystyrene (PS), polypropylene (PP), and poly(methyl methacrylate) (PMMA) [24–28]. The poly(vinylidene fluoride) (PVDF) stands out among these polymers because of its relative high dielectric constant (~10 at room temperature) due to its spontaneous polarization and excellent tunable electrical property [8]. In terms of conductive filler, the nickel crystallites can be an ideal candidate due to their inoxidizability, corrosion resistance and thermostability. According to the previous research [1,29], the nanometer scale $Ba(Fe_{0.5}Nb_{0.5})O_3$ crystallite (BFN) is an excellent candidate as the ceramic filler in PVDF and the optimum addition is fixed at 50 vol.%. The dielectric constant of this component is 77 and the loss is 0.18 at 100 Hz.

In this study, we report the details pertaining to the nanometer scale $Ba(Fe_{0.5}Nb_{0.5})O_3$/Ni/poly(vinylidene fluoride) three-phase composites associated with high dielectric constant and low dielectric loss. Meanwhile, two-phase composites comprising PVDF and Ni were also prepared for a comparative research. The structure, microstructure, electrical properties and dielectric properties of the PVDF based composites are discussed in detail.

2. Experiments

2.1. Materials

The poly(vinylidene fluoride)(PVDF), molecular weight of MW 534,000 supplied by Sigma-Aldrich was used in this study. Nickel powders (Ni, crystallite size ~ 5 μm), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), barium nitrate ($Ba(NO_3)_2$), oxalic acid ($(COOH)_2 \cdot 2H_2O$) and aqueous ammonia ($NH_3 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Niobium chloride was supplied by Alfa Aesar Co., Ltd. All chemicals used in the experiments were in analytical reagent grade and used as received without further purification.

2.2. Preparation of PVDF based composites

The nanometer scale $Ba(Fe_{0.5}Nb_{0.5})O_3$ powders were synthesized by oxalate coprecipitation method which could obtain smaller crystallites size than the conventional solid-state reaction. Ferric nitrate, barium nitrate and oxalic acid were dissolved in distilled water and niobium 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 950 °C for 2 h to obtain the nanometer scale BFN powders.

For the fabrication of Ni/PVDF composites, the Ni powders were mixed with PVDF powders by vibro-milling for 1 h. At this step, the volume fraction of Ni powders was varied from 5 vol.% to 25 vol.%. For the fabrication of BFN/Ni/PVDF three-phase composites, the nano-BFN ceramic fillers and Ni conductive fillers were mixed with PVDF powders by vibro-milling for 1 h. At this step, the volume fraction of Ni powders was varied from 20 vol.% to 25 vol.%, and the volume fraction of BFN ceramic powders is fixed as 50 vol.% according to our previous research. The mixture powders were cold-pressed to disk-samples with 10 mm in diameter and 1.5 mm in thickness. Then the PVDF based composites samples were obtained by heating treatment at 180 °C for 2 h.

2.3. Characterizations

The X-ray diffraction (XRD) studies were carried out by a D/max-2200PC diffractometer with Cu Kα radiation in a wide range of 2θ ($10^\circ \le 2\theta \le 80^\circ$). The differential scanning calorimetry (DSC) was conducted using an STA 409 PC instrument under nitrogen atmosphere at the heating rate of 10 °C/min. The fractured surface morphology of the samples was examined by scanning electron microscopy (SEM, S-4800). For SEM imaging, composites samples are initially frozen in liquid nitrogen, then fractured and sputter-coated with a homogeneous gold layer. The dielectric properties of the composites were measured by employing an impedance analyzer (Agilent-E4980A) in the frequency range from 10^2 Hz to 10^6 Hz. Prior to measurement, a thin cover layer of Ag was coated on both sides of the samples.

3. Results and discussions

3.1. Ni/PVDF two-phase composites

X-ray diffraction analysis was carried out to examine the crystalline structure of the PVDF and Ni/PVDF two-phase composites. The XRD peaks in Fig. 1(a) indicate that PVDF is a semi-crystalline polymer with mixing phase of α and γ [30,31]. The positions and relative intensities of diffraction peaks of PVDF are the same as our previous reports [1]. In the case of XRD patterns of a pure Ni crystallites, the diffraction peaks observe at $2\theta = 44.5^\circ$, 51.8°and 76.4° are assigned to the planes (111), (200) and (220) reflections, respectively, of Ni (PDF: 04-0850). For Ni/PVDF composites with 5 vol.% Ni crystallites, both the diffraction peaks of Ni and PVDF can be observed, which indicates that no reaction took place between fillers and matrix during the heating treatment process. With increasing concentration of Ni crystallites, the intensity of diffraction peaks attributed to PVDF obviously decrease, which indicates that the averaged interplanar distance of polymer matrix increases due to the incorporation of Ni crystallites [32]. Therefore, the incorporation of Ni crystallites obviously influences the crystalline structure of PVDF matrix.

The DSC melting curves of the PVDF and Ni/PVDF two-phase composites from 100 to 190 °C are shown in Fig. 1(b). Only one melting peak at around 163 °C can be observed for the composites, which is the melting temperature (T_m) of the PVDF. The melting enthalpy (ΔH_m) takes great charges down to 5.37 from 17.16 J/g. After calculation, the degree of crystallinity (X_c) of PVDF in composites with various volume fractions of Ni is also given. The X_c is calculated by the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^* f_c} \tag{1}$$

where φ stands for the weight fraction of PVDF in composites, and ΔH_m^* is an ideal PVDF crystal with X_c of 100% (taken as 104.5 J/g) [33]. It is observed that the X_c of pure PVDF is larger than that of Ni/PVDF composites. And the X_c is falling with the increasing of the volume fraction of Ni. It is proved that Ni has an effect on the crystallinity of PVDF, which also can support the result of XRD.