



Dielectric behaviors of PHBHHx–BaTiO₃ multifunctional composite films

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ABSTRACT

Multifunctional polymeric composites were investigated for potential use in high energy storage capacitors and tissue engineering. The polymeric composites were fabricated by employing biodegradable polyester, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx), as the matrix. Ferroelectric BaTiO₃ ceramic powders were added to the composites as fillers. The dielectric spectroscopy of the composites was measured over a wide frequency range (10⁰–10⁷ Hz) from –100 to 60 °C. The composition dependent dielectric behavior was modeled by a self-consistent effective medium theory. A percolation threshold of 0.367 was observed in the composites. The glass transition relaxation of the composite was also discussed by comparing the popular Vogel–Fulcher–Tammann law with a new glass model. The composites show attractive ferroelectricity and piezoelectricity for biomedical applications.

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1. Introduction

Dielectric materials with high dielectric constants are widely required for applications in embedded capacitors and other charge-storage devices in microelectronics [1–3]. Ferroelectric ceramics are brittle and have high dielectric constant and low dielectric breakdown strength. In contrast, polymers are flexible and have high dielectric breakdown strength and low dielectric constant ($\epsilon' = 2\text{--}5$) [4,5]. Therefore, there have been a lot of attempts to develop polymer-based composites to realize flexible materials for higher energy density which is proportional to dielectric constant but to the square of dielectric breakdown strength. In order to achieve such an objective, insulating ferroelectric powders such as BaTiO₃ (BTO), Ba_{1-x}Sr_xTiO₃ (BST), Bi_{0.5}Na_{0.5}TiO₃ (BNT), Pb(Mg_{1/3}Nb_{2/3})O₃–PbTiO₃ (PMN–PT) and PbZr_xTi_{1-x}O₃ (PZT) have been used as fillers to develop polymer–ceramic 0–3 composites [6–10]. Another strategy to raise the dielectric constant of polymer-based composites is to fabricate percolative composite capacitors by using conductive or semiconductive fillers [11,12].

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) is a kind of biodegradable copolyesters. The chemical structure of PHBHHx consists of 3-hydroxybutyrate (HB) and randomly distrib-

uted 3-hydroxyhexanoate (HHx) units [13], as shown in Fig. 1. The dielectric relaxation spectroscopy of PHBHHx has been reported in our previous work recently [14]. And besides its excellent thermal and mechanical properties [15,16], PHBHHx exhibits a relative high dielectric constant ($\epsilon' = 5$) [14]. Barium titanate, BaTiO₃ (BTO) [17,18], is a ferroelectric oxide with a perovskite structure and has very high dielectric constant ($\epsilon' > 1000$). In recent years it has been utilized for preparation of composites with various polymers, such as, poly(vinylidene fluoride) (PVDF) and its copolymers [19].

On one hand, PHBHHx has good piezoelectricity and biocompatibility and it also promotes cell growth for tissue engineering applications [20–22]. On the other hand, BTO has also attracted particular attention in bio-medical science, such as bone remodeling due to its piezoelectricity [23,24]. To further extend the range of application, BTO will be added into the PHBHHx matrix since it has a higher dielectric constant and better piezoelectricity. In the present work, we focused on the dielectric behaviors of PHBHHx/BTO composite. The piezoelectricity and ferroelectricity of this composite were also studied for the purpose of possible applications in tissue engineering. The multifunctional composite may also be employed as embedded capacitors and electronic elements for AC–DC conversion, etc.

2. Experimental

2.1. Materials and processing

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx, with HHx content of 12%) raw powders were kindly provided by

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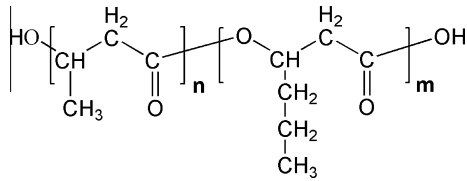


Fig. 1. Chemical structure of PHBHHx.

Jiangmen Center for Biotechnology Development, Guangdong, China. BaTiO₃ powders (<2 μm, AR) were purchased from Sigma-Aldrich.

The PHBHHx/BTO 0–3 composite films were fabricated by hot-pressing. First, the polymer powders were dissolved in acetone to form a solution and the BTO ceramic powders were then blended into the polymer solution. The mixture was ultrasonically agitated for uniform dispersion of the powder. Then MeOH was added under stirring to form uniform coprecipitation of the polymer–ceramic mixture. The mixture was dried at 50 °C overnight to evaporate the solvent. Finally, the dried mixture was cut into small pieces and compression-molded under a pressure of 20 MPa at 120 °C for 2 h. Composite films with different volume fraction of BTO (from 5% to 25%) were then obtained.

2.2. Scanning electron microscopy (SEM)

The morphology of the obtained films was observed with scanning electron microscope (SEM, JEOL JSM-6490). The composite film was fractured in liquid nitrogen and mounted on a metal pillar after sputter-coating with gold for 60 s. The acceleration voltage of the SEM apparatus was controlled at 20 kV. Thickness of the PHBHHx/BTO films was measured from SEM images and also by a Vernier caliper.

2.3. Dielectric relaxation spectroscopy (DRS)

For electrical measurement, silver was sputtered on both surfaces of the specimens. The dielectric properties and ac conductivity were measured by using a broadband frequency-response analyzer (Alpha analyzer, Novocontrol Technologies) over a frequency range of 10⁰–10⁷ Hz at various temperatures. The temperature was controlled by a Novocontrol Quatro Cryosystem with high accuracy (±0.1 K). The real and imaginary parts of dielectric constant [$\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$, where f is the frequency] were collected isothermally with increasing temperatures.

2.4. Ferroelectric hysteresis loop (P–E loop)

The polarization–electric field (P–E) hysteresis loop measurements were carried out using a modified Sawyer–Tower circuit at a frequency of 100 Hz. The piezoelectric constant d_{33} was measured after poling using a quasi-static d_{33} meter (Model ZJ-3A, China). The film was poled by means of a corona discharge in a point-to-plane corona. An electric field of 5 kV/mm was applied to the sample for 0.5 h at 50 °C.

3. Results and discussion

3.1. Morphology analysis

The uniform dispersion of fillers in a polymer matrix is very important for polymer–ceramic composites. In the current work, MeOH was used to achieve the homogeneous dispersion of BTO powders in PHBHHx polymer matrix. For comparison, Fig. 2 presents the SEM micrographs of the fractured surface of the

PHBHHx/BTO composites prepared with and without MeOH. It can be seen that, without MeOH, a large amount of BTO fillers were agglomerated at the bottom side of the film due to the precipitation of BTO during the solvent evaporation process. By adding MeOH into the polymer solvent, the BTO particles are homogeneously dispersed in the polymer matrix with an average size about 1–2 μm, suggesting little agglomeration.

3.2. Dielectric analysis

The room temperature dielectric constants of the PHBHHx/BTO polymeric composites with various volume fractions of filler were shown in Fig. 3. As expected, the effective dielectric constant increases with increasing BTO volume fractions. The measured value of ϵ' of the composite film containing 25% BTO is 20 at 1 kHz, much higher than that of the polymer matrix. Recently, the dielectric constant of poly(methyl methacrylate) (PMMA, $\epsilon' = 5$) composites with 30% surface-modified BTO particles was reported to reach 16 [25], which is lower than the current PHBHHx/BTO composite film. This may be due to the well-known “size effect” in BTO ferroelectric ceramics [26], where the dielectric constant of BTO (size ~1–2 μm) used in this study is much higher than that of the particles (size ~100 nm) used in Ref. [25].

From Fig. 3, it can be seen that addition of BTO did not change significantly the trend of frequency dependence of both ϵ' and $\tan \delta$ ($=\epsilon''/\epsilon'$). Furthermore, the dissipation factor $\tan \delta$ of the composites remained the similar frequency dependence as the polymer matrix did with two easily distinguishable regions. In region I (frequency <1 kHz), $\tan \delta$ decreases linearly with frequency, a behavior due to the dc conductivity and space charge effect [27,28]. In region II (frequency around 100 kHz), a loss peak was observed, characteristic of the α relaxation in polymers that is related to the segmental mobility. In addition, the $\tan \delta$ value increases first with increasing BTO up to 10% and then starts to decrease. Most importantly, $\tan \delta$ for all the composite films stayed below 0.1 in the frequency range of 10³–10⁷ Hz.

The theoretical understanding on the dielectric behaviors of composites is rather limited. For spherical fillers at relatively low volume fraction (<20%), the effective dielectric constant of composites can be described by a simple Maxwell–Garnett (MG) approximation [29],

$$\epsilon_{eff} = \epsilon_1 \left(1 + \frac{3V_2B}{1 - V_2B} \right) \quad (1)$$

where $B = (\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1)$ ($B < 1$), V_2 is the volume fraction of the fillers, ϵ_1 and ϵ_2 are the dielectric constants of the matrix and the fillers, respectively. However, the MG model does not take into account the influence of the particle–particle dipolar interactions and their effect on the surrounding medium. It is hard to reasonably predict the dielectric properties of composites at relative high volume fraction of the filler. Fig. 4 illustrates the simulated results according to the MG equation with $B = 1$, $\epsilon_1 = 5.2$ and $\epsilon_2 = 5000$. It can be seen that the experimental dielectric constants increase more rapidly than that predicted by the MG theory. Similar results have also been observed in many other polymeric composites, such as PVDF/CaCu₃Ti₄O₁₂ nanocomposites [30].

Recently, Li et al. [31,32] proposed a self-consistent effective medium theory (SC-EMT) to calculate the effective dielectric constant of composites over a wider range of volume fraction of the fillers. The effective dielectric constant ϵ_{eff} is expressed as

$$\epsilon_{eff} = \epsilon_1 + V_2(\epsilon_2 - \epsilon_1)a_2 + V_3(\epsilon_3 - \epsilon_1)a_3 \quad (2)$$

where the suffix 1, 2, and 3 represents the matrix, filler, and inter-phase, respectively, and a_r ($r = 2$ and 3) denotes the electric field concentration factor in each phase [31,32]. The effective medium

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