



A systematic study on electrical properties of the BaTiO₃-epoxy composite with different sized BaTiO₃ as fillers



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ABSTRACT

The epoxy composites consisting of BaTiO₃ fillers with size of 100 nm and 200 nm were prepared, respectively. The thermo-mechanical and electrical properties of BaTiO₃-epoxy composites were investigated using complex permittivity, electric modulus and ac electrical conductivity. The effects of filler size on the structure, filler-matrix interface and properties were discussed. The Havriliak-Negami model was used to analyze the dielectric relaxation of composites. The results show that larger filler tends to exhibit enhanced dynamic modulus and higher T_g because of the increase of effective volume fraction. The tetragonal phase formation in the BaTiO₃ is important to achieve enhanced permittivity of the composite. The relaxation responses of composites revealed by electric modulus and complex permittivity show that the Maxwell-Wagner-Sillars (MWS) polarization and tetragonal phase transition of BaTiO₃ affect the dielectric responses of composites. The conduction process is not only related with the barrier hopping but also tunneling effect of electrons. Based on the electrical properties of BaTiO₃-epoxy composite with 100 nm BaTiO₃ at GHz, a compact band-pass filter with significant area reduction was designed and fabricated. The measured results show that the BaTiO₃-epoxy composite is promising for advanced wireless device applications.

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1. Introduction

During the past few years, the inorganic particles filled polymer composites have attracted considerable interest because of their good processability and tailorable characteristics by controlling the content of the filler [1–3]. Various nano-particles, such as TiO₂ [4], CaCu₃Ti₄O₁₂ (CCTO) [5], SrTiO₃ and BaTiO₃ [1,6] have been employed as fillers for high permittivity dielectrics. Among them, BaTiO₃ is one of the most popular fillers in polymer composites [7–9] for embedded capacitor application. The properties of the polymer composites depend strongly on the filler size, filler-matrix interface and loading of filler. Therefore, understanding these factors is important to achieve the desirable polymer dielectric material with high performance.

Previous work reported that there was a relation between the permittivity and grain size of BaTiO₃ ceramic [8–10]. It was generally recognized that the permittivity of BaTiO₃ increased with the increasing size of BaTiO₃ [11–16] and the permittivity of BaTiO₃ strongly depends on the grain size of the tetragonal phase

structure while it is almost independent of grain size of the cubic structure [17]. The internal stress resulting in lattice distortion plays an important role in size effects. However, there is no clear conclusion for the BaTiO₃-polymer composites. Mao et al. [11] have reported that the remanent polarization of BaTiO₃ particles increased as the size of BaTiO₃ particles increased from 25 to 500 nm and the permittivity of the BaTiO₃-PVDF composites exhibited a maximum value in the composites with BaTiO₃ nano-particle sizes of 80–100 nm and decreased again when the particle size was further reduced under 50 nm. However, Fan et al. [12] found that the values of permittivity for the PI matrix filled with the size of 30–50 nm BaTiO₃ particles were higher than that filled with 80 nm BaTiO₃ particles.

Moreover, some reports [10] indicated that the smaller fillers would bring the serious influence to the mechanical properties of polymer composite. Thus, it is desired to clarify the issue of size effect on the dielectric characteristics and dynamic mechanical properties of the BaTiO₃ polymer composites.

Although significant efforts have been made for improving the permittivity of the BaTiO₃-epoxy composite, the temperature and frequency dependent dielectric responses of the composites are not fully understood. In particular, it is important to precisely

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evaluate influence of filler on the relaxation processes of the polymer and the possible contributions from the Maxwell–Wagner–Sillars (MWS) interfacial polarization. Meanwhile, the dielectric losses of polymer composites are mainly associated with the electrical conductivity of the polymer matrix and the polymer/nanoparticles interface effects. Therefore, understanding the conduction mechanism in the polymer composite system is important to realize the relaxation process of polymer composite.

For the practical application, the dielectric characteristics at near or over one gigahertz are important for wireless communication applications. Meanwhile, much work [18,19] has been focused on the embedded planar capacitor. However, there are few reports on the fully embedded VHF (very high frequency) band-pass filters using BaTiO₃–epoxy composites. In this paper, BaTiO₃–epoxy composites with the same BaTiO₃ volume concentration and different particle size were prepared. The influences of particle size, temperature and frequency on the dielectric properties and relaxation processes were evaluated by using complex permittivity and electrical modulus. The Havriliak–Negami model was used to figure out the contributions from interfacial polarization and conductivity. The conduction mechanism was analyzed by overlapping large polaron tunneling model. Specifically, based on the BaTiO₃–epoxy composite film, an embedded VHF band-pass filter was designed and fabricated, to extend the usable fields of BaTiO₃–epoxy composites.

2. Experiments

2.1. Preparation of BaTiO₃–epoxy composite film

The bisphenol F type epoxy resin (Bluestar New Chemical Materials Co., China), BaTiO₃ (100 nm, 200 nm, Guangdong Fenghua Advanced Technology Co., China), dicyandiamide, imidazole, and 2-butanone were used as the polymer matrix, dielectric filler, curing agent, catalyst and solvent, respectively. Dispersing agent (Hypermer PS3) was used to improve the dispersion of BaTiO₃ in the epoxy matrix. The following procedure independent of the particle size was used: 20 g of epoxy resin was dissolved in 160 g 2-butanone. Then, 100 g of barium titanate powder, and 6 g dispersing agent were added. The mixture was ultrasonically agitated for 2 h to obtain the mixture A. Then, 6 g dicyandiamide and 6 g imidazole were dissolved in 5 ml N, N-Dimethyl formamide solvent to obtain the mixture B. The mixture B was added in the above mixture A. The mixture was ultrasonically agitated for 2 h to obtain the stable and uniform slurry. The prepared slurry was coated on copper foil with a scratch coating method and heat-treated at 120 °C for 5 min to remove residual organic solvents. Two pieces were laminated face to face and cured at 190 °C for 2 h. The thickness of the dielectric film is ranged from 8 μm to 22 μm, which is determined by the demands.

2.2. Fabrication of embedded band-pass filter

In a typical process, one side of the layer capacitor (Cu/BaTiO₃–epoxy/Cu) electrode was selectively etched by an identical photolithography process for the preparation of capacitor laminates. The etched side of the capacitor core was then laminated with a layer of prepreg dielectric material. This was followed by etching the second capacitor electrode and subsequent lamination with another prepreg dielectric. Top and bottom capacitor electrodes were connected through microvia (conductive holes) to make the filter operational.

2.3. Characterization techniques

The crystal structure of BaTiO₃ was analyzed using X-ray diffraction (XRD, D/max-2500/PC, Rigaku Co.) with Cu Kα radiation, at a scanning speed of 2°/min in steps of 0.02°. The cross-section of the composite film samples was examined by scanning electron microscopy (Nova Nano SEM450, FEI). The thermal stability of the BaTiO₃–epoxy composites were investigated by dynamic mechanical analysis (DMA, Q800, TA Instruments) with a frequency of 1 Hz, a heating rate of 3 °C/min and under flowing N₂ atmosphere in a temperature range from 30 to 180 °C.

The frequency dependencies of the dielectric permittivity and loss tangent of the composites were measured by employing an Impedance Analyzer (Agilent 4294A) in a frequency range of 100–10⁶ Hz. The microwave dielectric properties of the composite were measured using resonant cavity method combined with a Vector Network Analyzer (Agilent 8722ES). In the resonant cavity technique, the resonant frequency and the quality factor of the empty cavity and materials were different. The relative permittivity and dielectric loss of the samples can be estimated from the shift in the resonant frequency and change in the Q of the system using the following equations:

$$\varepsilon_r' = \left(\frac{\phi_c(f_c - f_s)}{2\phi_s f_s} \right) + 1 \quad (1)$$

$$\varepsilon_r'' = \frac{\phi_c}{4\phi_s} \left(\frac{1}{Q_s} - \frac{1}{Q_c} \right) \quad (2)$$

$$\tan \delta = \frac{\varepsilon_r''}{\varepsilon_r'} \quad (3)$$

where ε_r' is the real permittivity and ε_r'' is imaginary permittivity. f_c is the resonant frequency of the empty cavity, f_s the resonant frequency of the cavity with sample, ϕ_c the volume of the cavity, ϕ_s the volume of the sample, Q_c the quality factor of empty cavity, and Q_s the quality factor of the sample. The fabricated band-pass filter was measured using a Network Analyzer (Agilent N5244A) and coplanar ground-signal-ground probes with a 500 μm pitch size.

3. Results and discussions

3.1. Characterization of BaTiO₃ and BaTiO₃–epoxy composites

Fig. 1 shows the X-ray diffraction patterns of the BaTiO₃ with size of 100 nm and 200 nm. It indicates that the BaTiO₃ material is in good agreement with the conventional tetragonal structure with the P4 mm space group (JCPDS No. 05-0626), with no impurity peak appearing in the diffractogram. The 200 nm BaTiO₃ powders show peak splitting at 45° corresponding to the (hkl) Miller index {002} and {200}, whereas 100 nm BaTiO₃ powders has one single peak at 45.3° corresponding to {200}. In general, the cubic BaTiO₃ (JCPDS No. 31-0174) has one single peak at 44.9° corresponding to {200}. Therefore, it can be concluded that the BaTiO₃ powders with size of 100 nm and 200 nm show a pseudo cubic and tetragonal-dominant structure, respectively.

Fig. 2 presents the SEM image of the fresh fractured cross section of the BaTiO₃–epoxy composites. Fig. 2(a) is the microstructure of pure epoxy which shows large-scaled lamellar structures. Fig. 2(b) is the images of the composite filled with 40 vol% 100 nm BaTiO₃ fillers. It presents some honeycomb structure because of the fillers falling from the epoxy matrix, and the fillers are homogeneously dispersed in the epoxy matrix. Fig. 2(c) is the cross section of the composites with 40 vol% 200 nm BaTiO₃. The BaTiO₃ particles are surrounded by the epoxy matrix. The observed morphologies would be used to explain mechanical properties of the composite. According to the earlier work by other researchers [20–22], the filler size, microstructure of composite and the interface between the fillers and matrix would affect the mechanical properties of the composite.

3.2. Thermo-mechanical properties of composites

Fig. 3 shows the storage modulus E' , loss modulus E'' and damping (E''/E') of BaTiO₃–epoxy composites obtained from the DMA analysis. The addition of nano-sized BaTiO₃ dramatically enhances the value of E' , E'' and damping of the composites in the glassy state

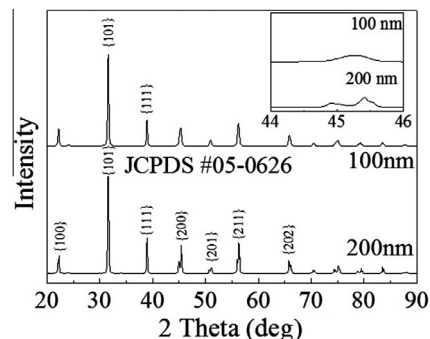


Fig. 1. X-ray diffraction patterns of BaTiO₃ with particle size of 100 nm and 200 nm. The inset shows the {200} reflection of BaTiO₃ powders.

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