

Effect of BaTiO₃ size on dielectric property of BaTiO₃/PVDF composites

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Abstract The BaTiO₃/polyvinylidene fluoride (BaTiO₃/PVDF) polymer-based composites with different size and concentration of BaTiO₃ particles were fabricated via a simple physical mixing and subsequently hot-press processing. Effect of the filler size and frequency on the dielectric properties of the BaTiO₃/PVDF binary composites was discussed. The result shows that the BaTiO₃ size has an effect on the morphology of the BaTiO₃/PVDF composites. The composites with 0.2 and 0.3 μm BaTiO₃ exhibit high dielectric permittivity than those with 0.4 and 0.5 μm BaTiO₃. The composite with 0.4 μm BaTiO₃ has a minimum dielectric permittivity except one with 0.1 μm BaTiO₃. Dielectric loss of the BaTiO₃/PVDF binary composites changes slightly with the BaTiO₃ sizes. The ternary BaTiO₃/PVDF composites with 0.1 and 0.7 μm BaTiO₃ in coexistence exhibit good dielectric properties. As a result, the BaTiO₃/PVDF ternary composites in this study may have a promising application as dielectric material in embedded capacitor.

Keywords BaTiO₃ size · Composite · Dielectric property

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1 Introduction

Electronic ceramic BaTiO₃ has been utilized as an excellent dielectric material in electronic industry. But BaTiO₃ ceramic needs to be sintered at a high temperature, which process consumes vast power. In addition, the ceramic materials have lots of disadvantages, such as poor flexibility which are not well satisfied for fabrication of electronic devices. To address these issues, ceramic/polymer composites have been evaluated as candidate dielectric materials for new-type capacitors, since the combination of polymer and ceramic may give the composites some advantages from both sides by a careful design and preparation.

Although the composites employing conductive fillers have made promising progress in the dielectric property [1–5], ceramic/polymer composites are still attractive to researchers because of simple and convenient process, cheap cost and excellent property, such as low dielectric loss, low conductivity and leakage current. In these studies [6–11], different systems have been demonstrated in order to obtain the desirable dielectric materials. In order to reach well-balanced properties between high dielectric constant and low leakage current, proper particle size elected for embedded capacitors is 0.5–0.7 μm in diameter [8]. Recently, nano-sized ceramic powers has been utilized in order to increase packing density resulted in higher permittivity and to decrease film thickness of ceramic/polymer composites used in embedded capacitor [7, 10]. It is also universally acknowledged that the dispersion of ceramic filler within the polymer matrix is a technical barrier for ceramic/polymer composites. Although many formulation factors and process factors could affect the particle dispersion, the use of coupling agent, dispersant and surfactant have been found to be an effective approach for improving dispersion [9, 12]. At present, improving the dispersion of ceramic filler within

the polymer matrix, together with increasing the permittivity of the polymer used in the composite, are the usual ways to obtain permittivity as high as possible.

In this paper, effect of BaTiO₃ size on dielectric property of the binary BaTiO₃/PVDF composites was discussed. The dielectric property of ternary composites with two kinds of BaTiO₃ in diameter as a function of ceramic concentration was investigated.

2 Experimental procedure

Two kinds of composites were preparation in this study. One is binary BaTiO₃/PVDF composites which were obtained by with one size BaTiO₃ power. The other is ternary BaTiO₃/PVDF composites which were obtained by with two kinds of BaTiO₃ in diameter (0.1 and 0.7 μm). The volume ratio of BaTiO₃ with different diameter was designed as 4:1. All kinds of BaTiO₃ powders were from Guoteng Electronic Ceramic Company and PVDF, Shanghai 3F company, China.

These powders were mixed by a simple physical mixing. The BaTiO₃/PVDF mixtures were then hot-pressed at 200°C and a desired pressure into disk-shape samples of about 12 mm in diameter and 1.2 mm in thickness. Ceramic loading of 10, 40, 60 vol.% in binary composites and ceramic loading of 30, 40, 50, 60, 70 vol.% in ternary com-

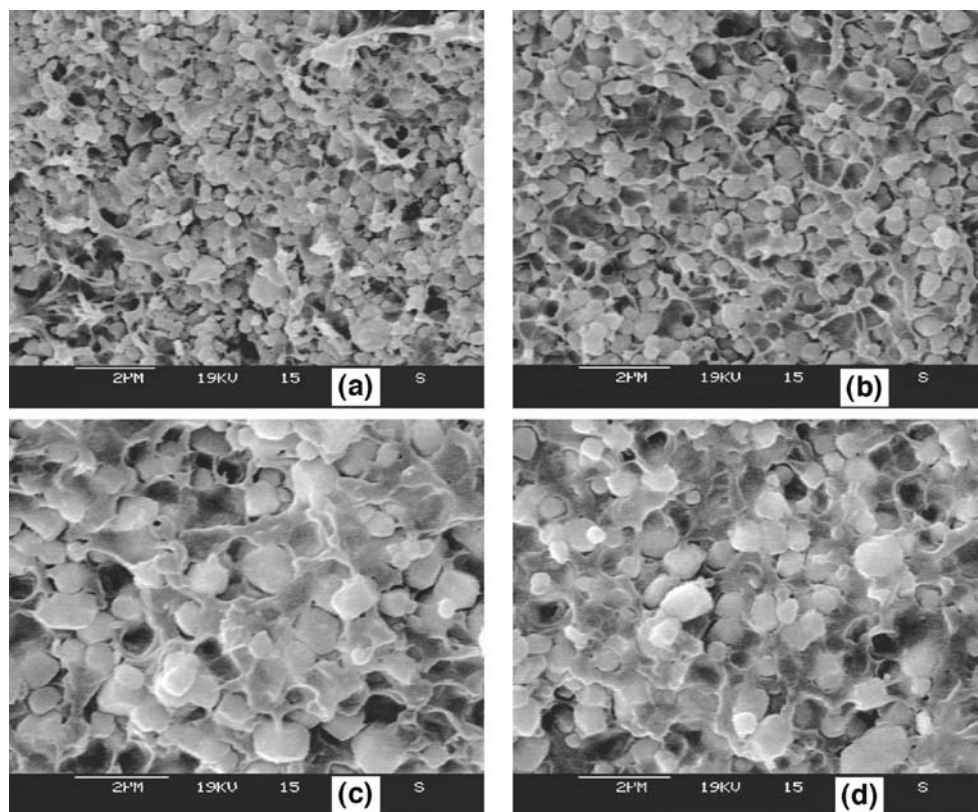
posites were prepared. The capacitance and tanδ values of the thick films were measured in frequency range from 1 kHz to 40 MHz by employing a HP 4294 A impedance analyzer at room temperature. The morphology of cross section of the samples was observed by scanning electron microscopy (SEM, JSE-6301F).

3 Results and discussion

Figure 1 shows cross section images of the binary BaTiO₃/PVDF composites (40 vol.% BaTiO₃) with 0.2, 0.3, 0.5, 0.7 μm ceramic powders, respectively. In Fig. 1(a), BaTiO₃ particles are self-connected into a continuous random cluster although there is a small quantity of BaTiO₃ aggregation. PVDF exhibits considerable phase separation. However, in Fig. 1(b),(c) and (d), the BaTiO₃ particles can be dispersed in continuous PVDF phase. It is clear that the size of BaTiO₃ has an effect on PVDF phase in the composites.

Frequency dependence of the dielectric permittivity of the binary composites with BaTiO₃ loading volume fraction at 0.10, 0.40 and 0.60 are shown in Fig. 2, respectively. It can be found that dielectric permittivity of the binary composites at the same ceramic loading volume has no simple change with ceramic size. The composites (10 vol.% BaTiO₃) with 0.1, 0.2 and 0.3 μm BaTiO₃ show higher dielectric permittivity than other. But at 40 vol.% BaTiO₃,

Fig. 1 Cross-section images of the binary composites with different size BaTiO₃ powders at a ceramic loading of 40 vol.%: (a) 0.20 μm; (b) 0.30 μm; (c) 0.50 μm and (d) 0.70 μm



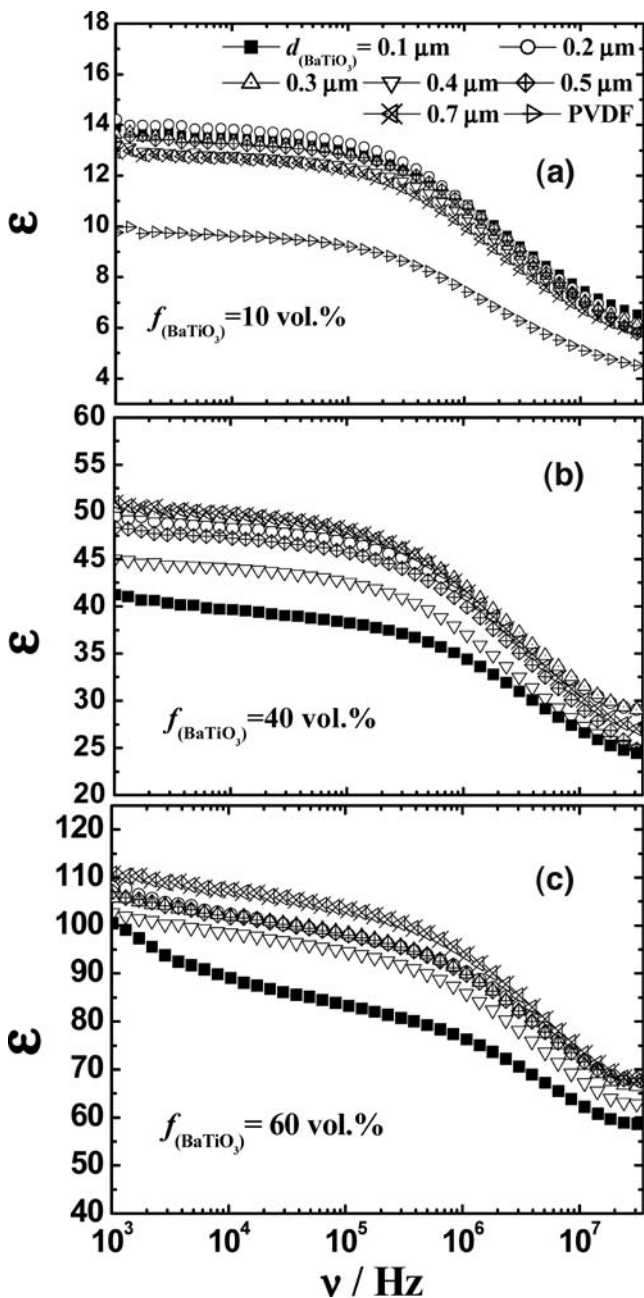


Fig. 2 Frequency dependence of dielectric permittivity of the binary BaTiO₃/PVDF composites with different size BaTiO₃ (a) 10 vol.%, (b) 40 vol.%, (c) 60 vol.% measured at room temperature

dielectric permittivity of the composites with 0.7 μm BaTiO₃ shows a maximum value in all composites, which can attribute to increase of dielectric constant of BaTiO₃ powders resulted from the increase of tetragonality phase [8] and occurrence of cluster structure of BaTiO₃ [13]. As the ceramic loading volume increase, the dielectric predominance of the composite with 0.7 μm BaTiO₃ is more obvious. However, it should be noted that in Fig. 2, dielectric permittivity of the composites with 0.2 and 0.3 μm BaTiO₃ are higher than those with 0.40 and 0.50 μm BaTiO₃. According to Fig. 1, it is assumed that

there is more chance for BaTiO₃ particles to form a continuous random cluster with the decrease of BaTiO₃ size, which might induce to form small aggregated cluster structure at relatively low loading volume of BaTiO₃. As a result, the dipole-dipole interaction increases and contributes to higher dielectric permittivity. In addition, the composite with 0.4 μm BaTiO₃ has lower dielectric permittivity than other composites, except the composites with 0.1 μm BaTiO₃ which has the lowest dielectric constant in all composites at ceramic loading of 40 and 60 vol.% due to the cubic structure of 0.1 μm BaTiO₃.

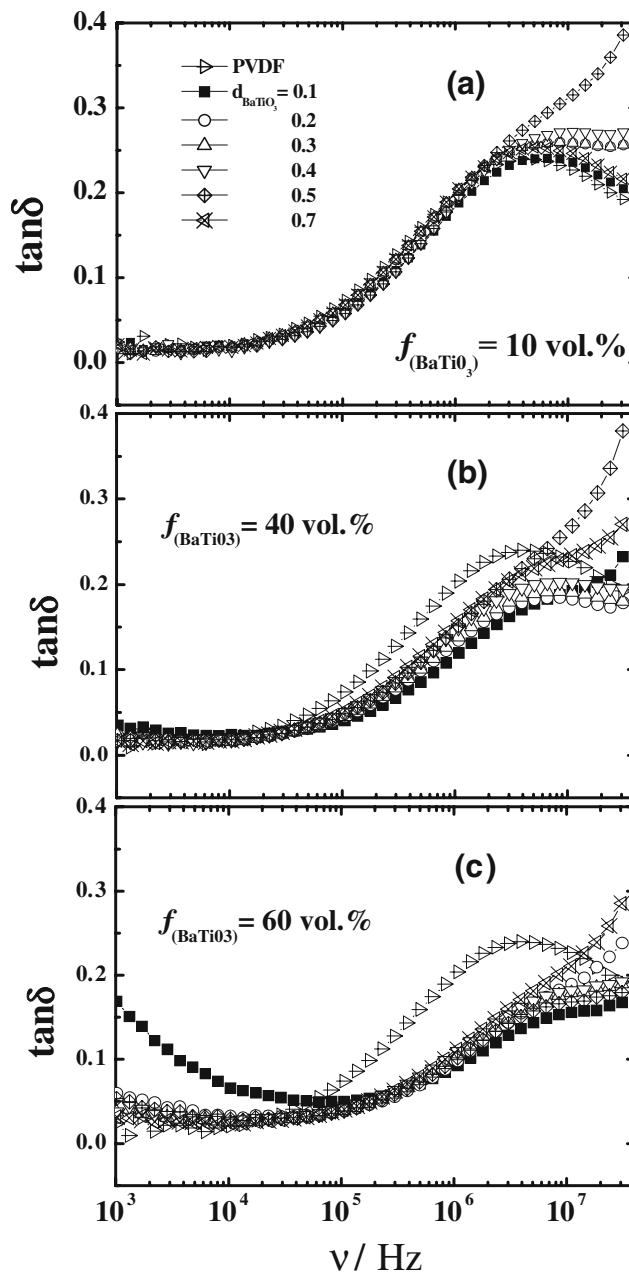


Fig. 3 Frequency dependence of dielectric loss of the binary BaTiO₃/PVDF composites with different size BaTiO₃ ; (a) 10 vol.%, (b) 40 vol.%, (c) 60 vol.% measured at room temperature

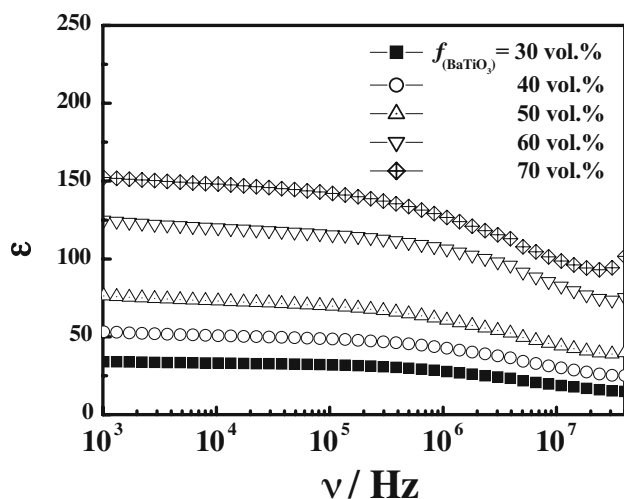


Fig. 4 Frequency dependence of dielectric permittivity of the BaTiO₃/PVDF ternary composites with different BaTiO₃ volume fraction measured at room temperature

Dependence of dielectric loss of the binary composites with different size BaTiO₃ on frequency at room temperature is shown in Fig. 3. It can be found that the binary composites exhibit a similar dielectric loss behavior as the BaTiO₃ loading volume increases at the measured frequency of less than 3 MHz. When the frequency is lower than about 20 kHz, dielectric loss of the binary composites is higher than that of PVDF. In particular, the binary composites with 0.1 μm BaTiO₃ show higher dielectric loss than those with other size BaTiO₃ at ceramic loading of 40 and 60 vol.%. Even with 60 vol.% BaTiO₃, the dielectric loss value of the binary composite with 0.1 μm BaTiO₃ is more than 0.06, which can not fulfill the requirement of the embedded capacitor application. It is clear that the volume fraction of 0.1 μm BaTiO₃ has a heavy effect on dielectric loss of the composites in frequency range of lower than about 20 kHz. When the frequency measured is more than about 20 kHz, the dielectric loss values of the binary composites decrease as BaTiO₃ volume fraction increases and the BaTiO₃ size decreases, especially for the composite with 0.1 μm BaTiO₃.

Figure 4 shows frequency dependence of dielectric permittivity of the ternary BaTiO₃/PVDF composites with different loading volume of BaTiO₃ at room temperature. In the measured frequency, compared with in Fig. 2, the dielectric permittivity of the ternary composites is higher than those of the binary composites at same loading concentration. The dielectric permittivity value of 76.23 at 1 kHz and 69.57 at 100 kHz are achieved at 50 vol.% BaTiO₃. And the maximum value of the dielectric permittivity in this work reaches to 152.25 at 1 kHz and 142.08 at 100 kHz irrespectively at 70 vol.% BaTiO₃. It can also be found that when the loading volume of BaTiO₃ ranges from

50 to 60 vol.%, the value of the dielectric permittivity increases rapidly. The increasing value of dielectric permittivity is about 45 in frequency range of less than 1 MHz. Maybe it is because that pores in the ternary composites between BaTiO₃ and PVDF are much less than that in the binary composite, which could be attributed that the particles of 0.1 μm BaTiO₃ fill the interstitial space between 0.7 μm BaTiO₃ and PVDF. As we know, the pores are unable to contribute to the increase of dielectric permittivity. Furthermore, the main reason is likely due to the fact that more ceramic particle can contact each other and the dipole-dipole interaction increases.

4 Conclusion

The size of BaTiO₃ particle has an important effect on dielectric permittivity of the BaTiO₃/PVDF composites studied in this study, which results from the change of the microstructure of the BaTiO₃/PVDF composites when the BaTiO₃ with different sizes is utilized. Dielectric loss values of the binary composites have slight change with the size of BaTiO₃. But the volume concentration of 0.1 μm BaTiO₃ has heavy effect on dielectric loss of the composites in frequency range of lower than about 20 kHz. The BaTiO₃/PVDF ternary composites exhibit higher dielectric permittivity than binary composites. The reason for the result is related to the less porosity and more dipole-dipole interaction in the ternary composites. As a result, the BaTiO₃/PVDF ternary composites in this study can be a promising material deserving to investigate for embedded capacitor further.

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