Effect of the Ceramic Particle Size on the Microstructure and Dielectric Properties of Barium Titanate/Polystyrene Composites

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ABSTRACT: Excellent dielectric properties are a key factor for the technology of capacitors. Some ceramics, such as barium titanate (BaTiO$_3$ or BT), have high dielectric constants, although they are hard to process. Polymers that often display low dielectric permittivities are easy to fabricate into all kinds of shapes. So the preparation of one composite material consisting of polymer and ceramic particles may be an excellent solution for satisfying the processing requirements. In this study, fresh polystyrene (PS) was synthesized and subsequently used to prepare BT/PS composites with a ball-grinding mixture technology. The microstructure and dielectric properties of the BT/PS composites at different frequencies and different temperatures were studied. The results show that the dielectric permittivities of the composites with BT with a particle diameter of approximately 700 nm (BT-07) were obviously higher than those of the composites with BT with a particle diameter of approximately 100 nm (BT-01) at the same concentration of BT. Moreover, the dielectric permittivities of the composites with BT-01 displayed better stabilization than those made with BT-07 at the different temperatures. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3473–3479, 2008

Key words: blends; composites; heterogeneous polymers; matrix; microstructure

INTRODUCTION

Recently, extensive attention has been paid to the use of polymer–ceramic composites in embedded capacitor technology.[1–5] Important requirements for embedded capacitor materials include a high dielectric permittivity, good processability, low dielectric loss, and low cost.[2,3] However, no single material can meet all of these requirements. The composites exhibit different dielectric properties because of the difference in ceramic particles in the polymer hosts. Barium titanate (BaTiO$_3$ or BT) is a kind of nonconductive ceramic with a high permittivity, so by changing the filler content of BT, we could adjust the dielectric properties of the composites. However, the effect of the particle size of BT on the dielectric properties is very important. Numerous contributions have been devoted to the effect of BT particle size on the dielectric properties in the BT ceramic itself and in BT/polymer composites.[6–14] Some issues are still unclear because of a changes in the polymer hosts used, which often show different physical–chemical characteristics.

In bulk BT ceramics, grain size has a strong effect on the dielectric permittivity at room temperature for grain sizes below about 10 μm.[7,15] Dielectric permittivity increases with decreasing grain sizes up to a maximum of about 700 nm.[16] Below this size, the dielectric permittivity sharply decreases in conjunction with the reduction of the tetragonal phase and remnant polarization.[15] The crystal structure of BT powder changes with particle size. Below about 100 nm, the tetragonal phase disappears, which results in a cubic structure. Therefore, it can be expected that the dielectric permittivity of BT powder will vary with BT particle size.

The dielectric permittivity and the volume fraction of the ceramic used in the composites are key factors in the determination of the composite permittivity. Moreover, the dispersion of ceramic particles with a tetragonal structure in the polymer is an important

issue in the achievement of a high dielectric permittivity. Until now, the dielectric properties of BT/polystyrene (PS) composites have been studied little. In this study, PS was synthesized with emulsion polymerization, and subsequently, the fresh PS was used to prepare the BT/PS composites by a ball-grinding mixture technology. Our aim in this study was to fabricate BT/PS composites dense in microstructure with a concentration change of BT and research how their dielectric permittivities responded to changes in volume concentration and particle size of BT, frequency, and temperature.

EXPERIMENTAL

Raw materials

The key raw materials, BT powders and the styrene unit, used in our study are shown in Tables I and II, respectively. The dodecyl benzene sulfonic acid sodium salt ($C_{12}H_{25}C_6H_4SO_3Na$) used in this study was supplied by Shanghai Guoyao Chemical Limited Co. (Shanghai, China), and $K_2S_2O_8$ was supplied by the Third Chemical Factory of Tianjin (Tianjin, China).

Fabrication process of the BT/PS composites

The PS was synthesized with the emulsion polymerization of 6 g of styrene with 0.06 g of $K_2S_2O_8$ as an initiator and 2 g of $C_{12}H_{25}C_6H_4SO_3Na$ as an emulsion at 70°C for 6 h. After the PS was prepared, the compounding of the BT/PS composites was done by a ball-grinding mixture technology. The blend process was performed at room temperature and 500 rpm for 20 h. BT loadings of 40, 60, 70, and 80 vol % in the BT/PS composites were prepared. The BT/PS mixtures were compressed in a mold at room temperature and 25 MPa for about 20 min. Then, they were molded by hot pressing at about 150°C and 25 MPa for 30 min to ensure good compactness in the final composite samples. Figure 1 shows the schematic process of the preparation of the BT/PS composites.

Characterization of the BT/PS composites

Fourier transform infrared (FTIR) [Nicolet, USA] spectra (Nexus 670) were used to characterize the fresh PS. X-ray diffraction (XRD; D/Max 2500)

TABLE I
Specifications of the BT Powders

Powder	BaTiO$_3$
Manufacturer	Shandong Guoteng Ceramic Corp.
Diameter	100 or 700 nm
Density	5.85 g/cc
Ba/Ti ratio	~ 1 : 1

TABLE II
Specifications of Styrene

Molecular formula	C$_8$H$_8$
Manufacturer	Tianjin Yongda Chemical Research Center
Molecular weight	104.15
C$_8$H$_8$ content	≥98.0%
Relative density	0.906–0.909

[Rigaku, Japan] was used to identify the crystalline phase of the BT powder. The fractured surface morphologies of the BT/PS composites were investigated by scanning electron microscopy (SEM).

Dielectric measurements of the BT/PS composites

The alternating-current dielectric properties of the composite samples were measured with an Agilent 4294A (Agilent, USA) impedance analyzer in both the frequency range 10^2–10^6 Hz and the temperature range −50 to 50°C. Before measurement, the two sides of each samples were coated with silver paste for electrodes.

RESULTS AND DISCUSSION

FTIR spectra of PS and the BT/PS composites

Figure 2(a) shows the FTIR spectra of the fresh PS synthesized in this study. The characteristic peaks of PS were clearly observed in the spectra. The stretching vibration of C—H in benzene at both 3059.05 and
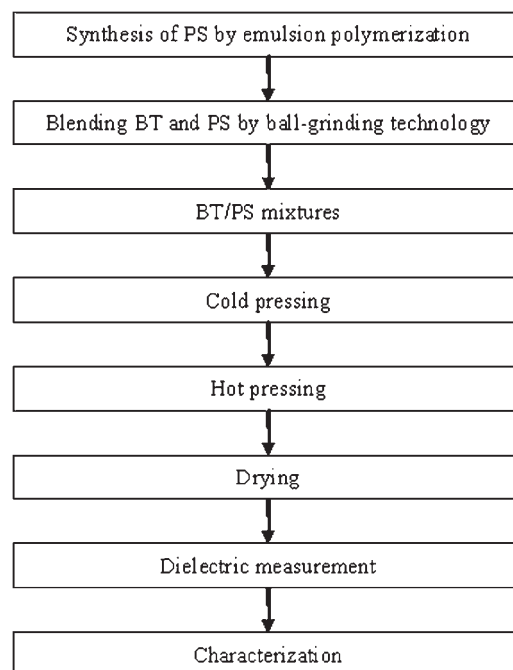

Figure 1 Flow chart showing the preparation process for the BT/PS composites.
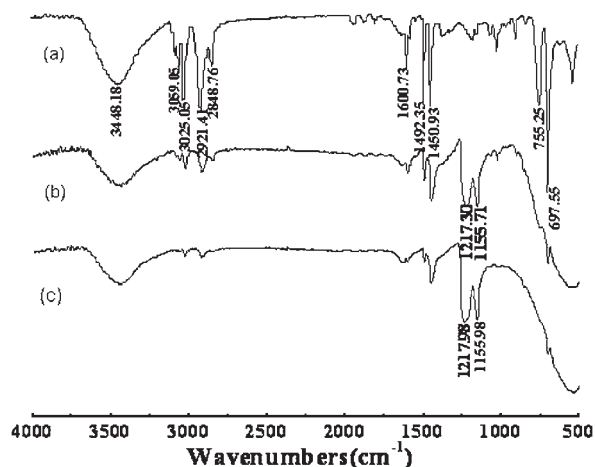
Figure 2 FTIR spectra of (a) pure PS, (b) the BT/PS composite with 40 vol % BT, and (c) the BT/PS composite with 60 vol % BT.

Figure 3 XRD patterns of BT-01, BT-05, and BT-07 powders.

3025.05 cm^{-1}; C=C, which belonged to the benzene stretching vibration at 1600.73 cm^{-1}; the aromatic C—H in-plane s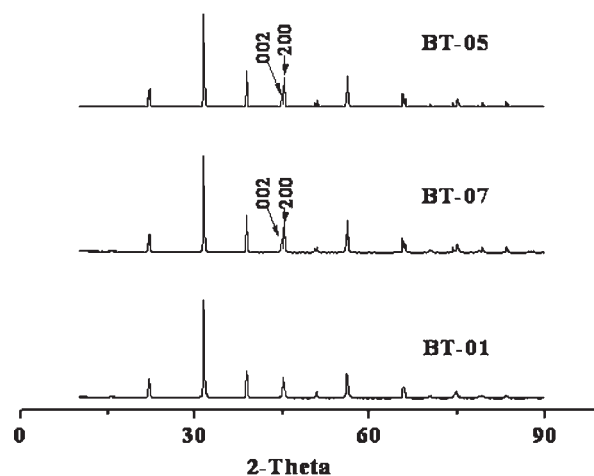tretching vibration at 1492.35 cm^{-1}; the C—H out-of-plane bending vibration at 755.25 cm^{-1}; and the aromatic C—C out-of-plane bending vibration at 697.55, 755.25, and 697.55 cm^{-1} are
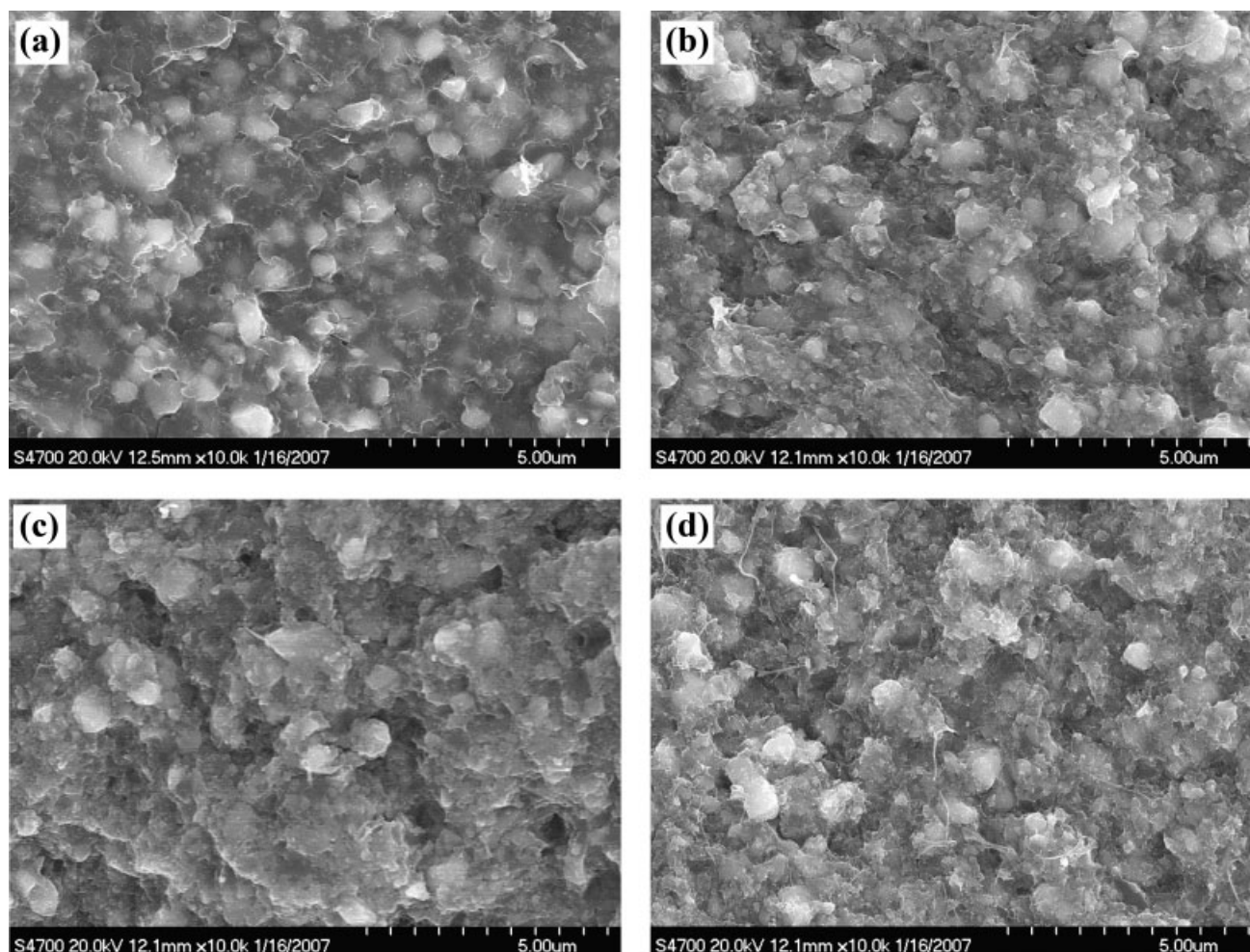

Figure 4 SEM photographs of the fractured surface of the BT/PS composites with BT-07 at (a) 40, (b) 60, (c) 70, and (d) 80 vol %.
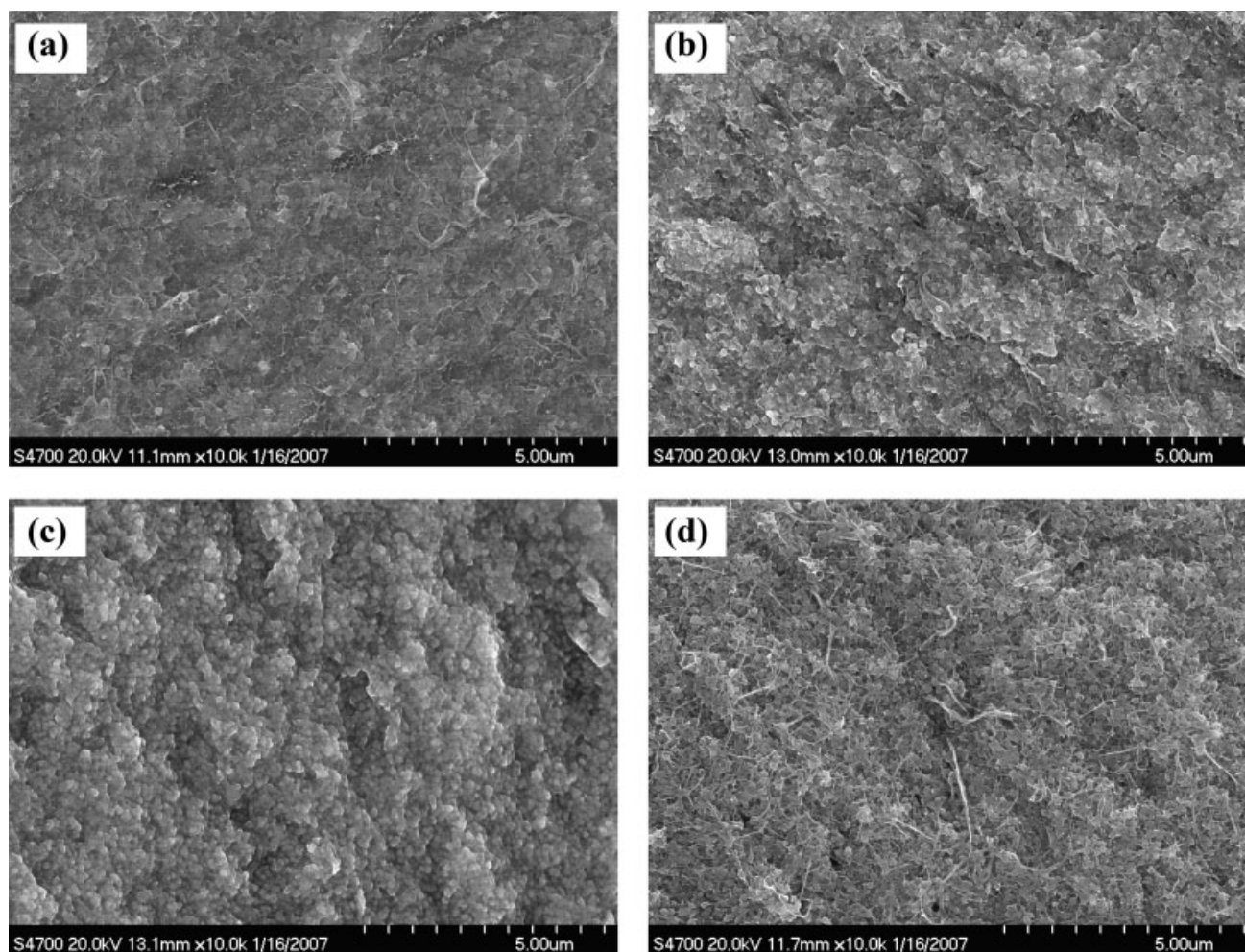
Figure 5 SEM photographs of the fractured surface of the BT/PS composites with BT-01 at (a) 40, (b) 60, (c) 70, and (d) 80 vol %.

characteristic peaks of benzene. Figure 2(b,c) presents the FTIR spectra of the BT/PS composites with BT (with a particle diameter of ca. 100 nm) loadings of 40 and 60 vol %. From the curves, we could easily find that most of the characteristic peaks of PS, such as at 3025.05, 2921.41, 755.25, and 697.55 cm^{-1}, were remarkably weakened or disappeared with increasing BT content. Moreover, compared with the FTIR spectra of PS, two FTIR spectra of the BT/PS composites showed two new characteristic peaks at 1217 and 1155 cm^{-1}. As we know, the C—H of the benzene in-plane bending vibration at 1217 cm^{-1} and the C—O stretching vibration at 1155 cm^{-1} would have appeared after the BT phase was introduced into PS because the chemical reaction between BT and PS might have been induced during the preparation process of the BT/PS composites.

XRD patterns of the BT samples

Particle size is an important factor in the dielectric permittivity of BT. Dielectric permittivity can go up

to a maximum at 700 nm, whereas it decreases sharply below this size because of the reduction of the tetragonal phase. Figure 3 shows the XRD patterns of three kinds of BT powders with particle sizes of 100 (BT-01), 500 (BT-05), and 700 nm (BT-07). As shown in Figure 3, the positions of the XRD peaks of BT-01 were similar to those of BT-05 and BT-07, but the tetragonal structure could be discriminated from the cubic structure by the peak split at $2\theta = 45°$. This region of the diffraction pattern is characteristic of the tetragonal phase of BT.[17] There was a split of the (200) reflection in the tetragonal phase, with the lower angle shoulder indexed as (002).[18]

Morphologies of the fractured surface of the BT/PS composites

In ceramic–polymer composites, the interface miscibility between the ceramic and polymer is very important, and it plays a crucial role in the microstructure and properties of the ceramic–polymer
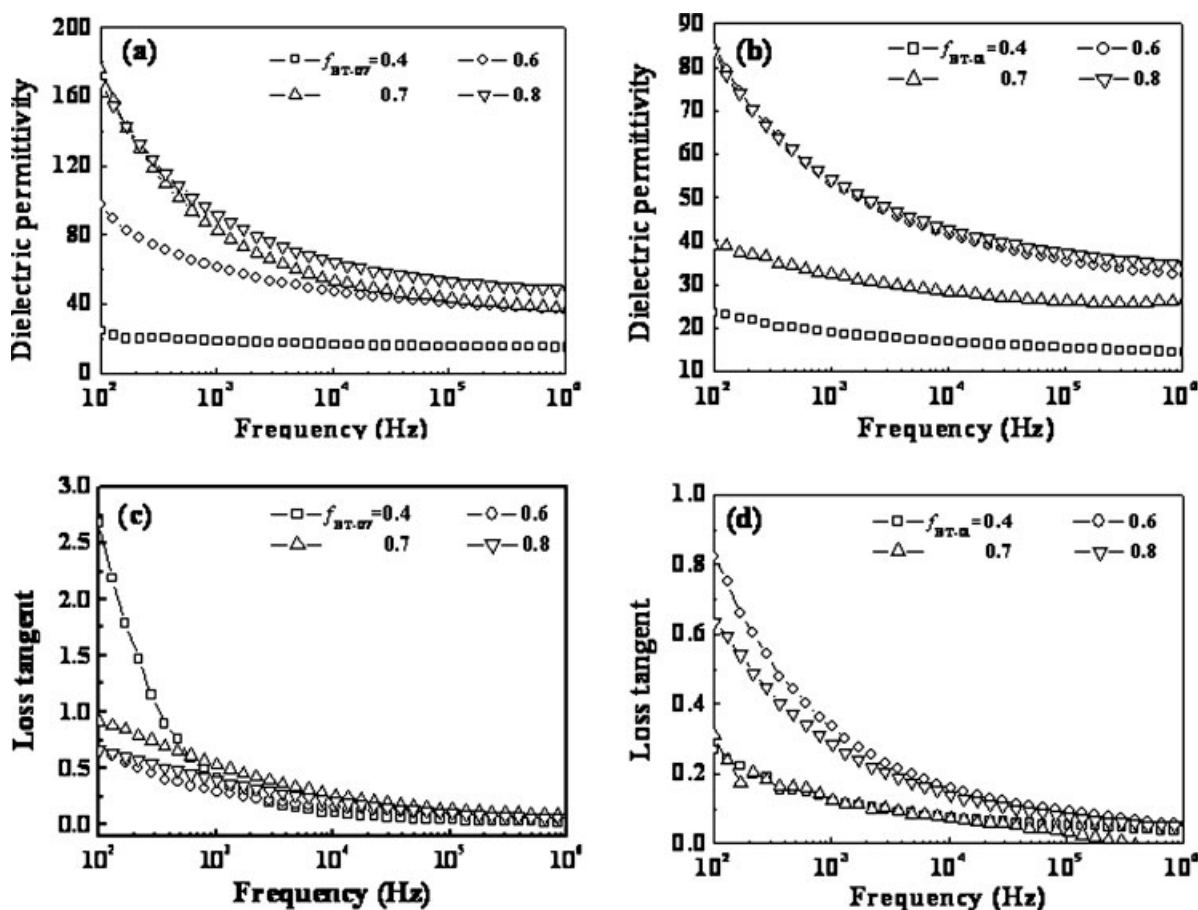
Figure 6 Frequency dependence of (a,b) the dielectric permittivity and (c,d) the loss tangent of the BT/PS composites with BT-01 and BT-07 at different concentrations.

composites. Figure 4 shows the morphologies of the fractured surfaces of the BT/PS composites with different BT contents and diameters. Figure 4(a–d) presents SEM photographs of the BT/PS composites loaded with BT-07 at 40, 60, 70, and 80 vol %, respectively. As shown by the SEM photographs, the holes and flaws in the materials became more sparse with increasing BT content. As shown in Figure 4(a), the BT-07, a particle about 700 nm in diameter, was dispersed into the PS matrix homogeneously, and the boundaries between the BT and PS were not very distinct. However, as shown in Figure 4(d), the fractured surface of the BT/PS composite at 80 vol % loading was not flat, and there were many holes in the visual surface. The main cause for this phenomenon was that the composite materials became less compact and easily brought out slots and holes with decreasing concentration of PS. Figure 5(a–d) presents SEM photographs of the BT/PS composites loaded with BT-01 at 40, 60, 70, and 80 vol %, respectively. The similar status mentioned previously also appeared in the fractured surface of the BT/PS composites with BT-01 loadings at 40 and 80 vol %, as shown in Figure 5(a,d), respectively.

Dielectric properties of the BT/PS composites

The dielectric properties of the BT/PS composites with different volume percentages of BT at different frequencies and at room temperature are shown in Figure 6. As we expected, the dielectric permittivities of the BT/PS composites with BT-07 were always larger those that of the BT/PS composites with BT-01 at the measurement frequencies. As the volume percentage of BT-07 increased, as shown in Figure 6(a), the dielectric permittivity of the composites increased as expected in the BT/PS composites because of high content of tetragonal structure in BT-07. However, this issue was different in the BT/PS composites with BT-01. As shown in Figure 6(b), at different frequencies, the dielectric permittivities of the BT/PS composites with BT-01 at 60 vol % were smaller than those with BT-01 at 80 vol % and larger than those with BT-01 at 70 vol %. The result could be understood as follows and was confirmed by some important information from the SEM photographs in Figure 5(c,d). Namely, although the ceramic content in the BT/PS composites with BT-01 at 70 vol % was higher than that with BT-01 at

60 vol %, when more ceramic was loaded, more holes existed in the composites. The existence of lots of holes affected the dielectric properties and resulted in lower dielectric permittivities. Moreover, the dielectric permittivity of BT-01 was not as high as that of BT-07; thus, the dielectric permittivity increase that resulted from a 10% increment of BT-01 seemed to be negligible. The new holes and flaws that were brought by the increase in ceramic were considered the main factors that lead to the weakening of the dielectric properties of the composites. When the ceramic content in the BT/PS composites with BT-01 continued to rise and reached a loading of 80 vol %, the dielectric permittivity increased remarkably, although many holes still existed in the BT/PS composites. We assumed that the effects of holes and flaws in the BT/PS composites were weakened correspondingly because of the increasing content of ceramic. However, this issue was different when the ceramic was BT-07. Compared with BT-01, the dielectric permittivity of BT-07 was much higher because of the crystal phase, so the increment of ceramic content was the crucial factor in the increase of the composite dielectric permittivity. Although the increasing ceramic content also resulted in new holes and slots, their effects on the BT-07/PS were also weakened just like those on the BT-01/PS composites with a BT-01 loading of 80 vol %. This may have been the main reason that the dielectric permittivity of BT-07/PS increased linearly with BT content, whereas BT-01/PS had a minimum at 70% content. In addition, the result that the dielectric permittivity of BT/PS composites with BT-01 was significantly lower than that with BT-07 under the same ceramic content was in accordance with the XRD analysis, which showed that the tetragonal phase was the main phase in BT-07, whereas the cubic structure was the main phase in BT-01, and the cubic phase was symmetrical and, therefore, a weak polarization. The dielectric loss tangents of the BT/PS composites with BT-01 and BT-07 are shown in Figure 6(c,d), respectively. Compared with the BT/PS composites with BT-01, the dielectric loss tangent of the BT/PS composites with BT-07 was a little large. The dielectric loss tangent values of the BT/PS composites with different BT volume percentages were mainly from 0 to 1, regardless of the diameter of the BT powders.

The temperature dependences of the dielectric permittivity of pure PS and the BT/PS composites at 10^6 Hz are shown in Figure 7. As shown in Figure 7(a,b), no matter what the diameter of BT was, 100 or 700 nm, the dielectric permittivity of the BT/PS composites moved to higher values with increasing temperatures, but the moves were not quite remarkable. Compared with the BT/PS composites with BT-01, the BT/PS composites with BT-07 showed a
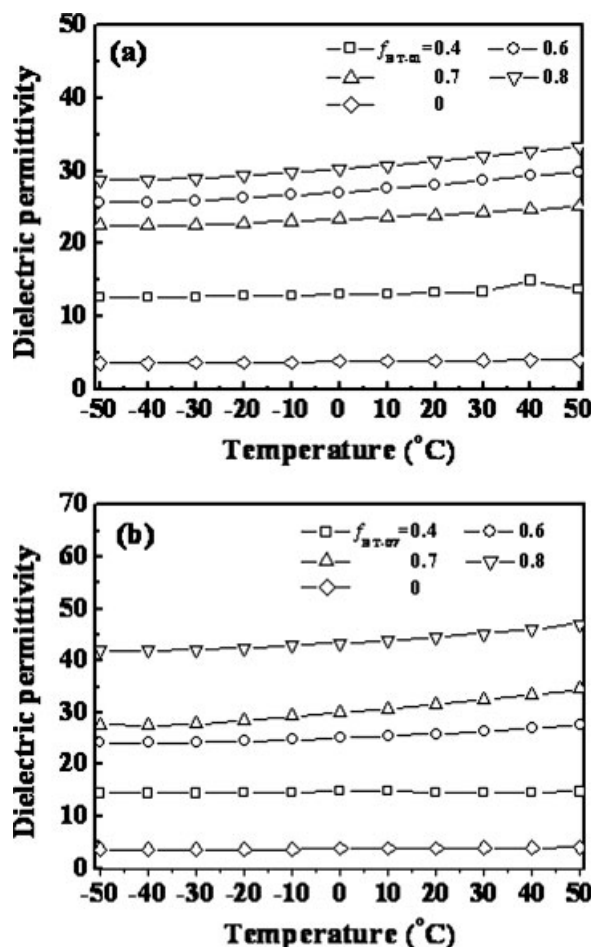

Figure 7 Temperature and concentration of the BT dependence of the dielectric permittivity of pure PS and the BT/PS composites with (a) BT-07 and (b) BT-01 at 10^6 Hz.

negligible temperature dependence. This process was mainly due to the transition of the crystal structure of BT and the enhancement of the particle movement ability. It is well known that the Curie temperature of BT is 120°C.[19] Below the Curie temperature, however, as the temperature varies from −50 to 50°C, there is another phase transition. Namely, the phase of BT transforms from the orthorhombic phase into the tetragonal one as the temperature increases and approaches −50°C. Compared with BT-07, the transition in which the orthorhombic phase transformed into the tetragonal one was more helpful for BT-01 to improve the polarization and, subsequently, result in an increase in dielectric permittivity. XRD patterns supported the result; namely, the phases of BT-01 and BT-07 were cubic and tetragonal, respectively, at room temperature. In addition, as the temperature increased, the enhancement of particle movement ability was another important factor, which often led to the polarization of ceramic powders and an increasing dielectric permittivity of the BT/PS composites.

CONCLUSIONS

Fresh PS was synthesized with emulsion polymerization and was used to prepare BT/PS composites with different BT diameters by a ball-grinding technology. Composites with BT-07 exhibited better dielectric properties than those with BT-01 under the same ceramic content over the wide frequency region. The values of dielectric permittivity increased with temperature regardless of the diameter of the BT powders. However, compared with the BT/PS composites with BT-07, the BT/PS composites with BT-01 showed a more obvious temperature dependence.

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