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Preparation and Dielectric Properties of $(Ba_{0.5}Sr_{0.4}Ca_{0.1})TiO_3$/Polystyrene Composites

Liang Zhang, Jun Zhao, Er-Quan Huang, Jun-Wei Zha, Zhi-Min Dang
Department of Polymer Science and Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, People's Republic of China
Correspondence to: Z.-M. Dang (E-mail: dangzm@ustb.edu.cn)

ABSTRACT: Polymer composites with polystyrene (PS) as matrix and $(Ba_{0.5}Sr_{0.4}Ca_{0.1})TiO_3$ (BSCT) as fillers are prepared by solution casting method. It is found that the dielectric constant of the prepared BSCT/PS composites increases with increasing filler content over the frequency range from 100 Hz to 500 MHz. And the dielectric properties of the composites show a good temperature independency over the range of −30°C to 80°C. For the composite with 50 vol % filler content, the dielectric constant and dielectric loss are comparable with the literature values reported for other PS composites used for microwave substrate. Several theoretical models are used to compare with the experimental data of the dielectric constant of the composites. The microstructure and thermal properties of the composites were also studied. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41398.

KEYWORDS: composites; dielectric properties; polystyrene

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INTRODUCTION

With the rapid growth of telecommunication systems and high-speed digital devices, researchers are stimulated to develop new high-performance dielectric materials. For high-frequency applications such as microwave devices, dielectric materials with suitable dielectric constant, low dielectric loss, and good temperature stability are required.[1] Up till now, such materials applied in microwave field are mainly ceramics, which have the disadvantages of high brittleness, challenging processing condition, and high density.[2] As an increasingly popular material, polymer has the merits of easy processing, high flexibility, and low density.[3] However, polymer also has the drawbacks of low dielectric constant, high thermal expansion, and low thermal conductivity. One way to combine the better aspects of both ceramics and polymers is to prepare composites with polymers as matrix and ceramics as fillers.[3–5] Ceramic-polymer composites have been seen as a group of materials which are suitable for functional and demanding electronic products.[6,7]

It is well known that the dielectric properties of the inorganic/polymer composite materials are determined by both the matrix and the fillers. Therefore it is very important to match appropriate polymers and inorganic fillers.[8] Many different kinds of polymers including thermosets and thermoplastics have been used as the matrix of dielectric composites, such as polyimide (PI), poly(vinylidene fluoride) (PVDF), poly(vinylidenefluoride-co-trifluoroethylene) (P(VDF-TrFE)), and polymethylmethacrylate (PMMA).[9–14] However, most of the polymers were investigated for the frequency below 10 MHz. For the applications in the microwave frequencies, the most widely used polymers are polyethylene (PE), polytetrafluorethylene (PTFE), and polystyrene (PS).[15–21] Among them, PS has unique excellent processing properties and low dielectric loss. Concerning the ceramics, $BaTiO_3$ (BT), $CaCuTi_4O_{12}$, $Pb(Zr,Ti)O_3$ (PZT), and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) are among the most widely used materials.[22–31] But most of them have relatively high dielectric loss (ca. 0.1–0.5). Preparation of core-shell structure has been used to decrease the dielectric loss. The strategy usually involves grafting the filler particles with polymer chains[32] or adding insulating inorganic layers such as aluminum oxide.[33] In addition, incorporating Sr or Ca element into BT to form $(Ba,Sr)TiO_3$ and $(Ba,Sr,Ca)TiO_3$ has already been found to enable the reduction of the dielectric loss of ceramics.[34,35] Especially, $(Ba_{0.5}Sr_{0.4}Ca_{0.1})TiO_3$ (BSCT) is one example with high dielectric constant of ca. 3200 and low dielectric loss of ca. 0.001–0.002 at room temperature and 2 MHz.[36]

Based on such background, BSCT/PS composites with various filler contents were prepared in this study. The dielectric properties were investigated to exam the possibility of applications of such composites in microwave frequency range. The experimental results of dielectric constant were compared with well-known theoretical models including Maxwell–Wagner equation, Lichtenecker equation, modified Lichtenecker equation. In addition, the microstructure and thermal properties of the composites were studied in order to further understand the BSCT/PS composites.

EXPERIMENTAL

Materials

$CaCO_3$ (99%), $BaCO_3$ (99%), $SrCO_3$ (99%), and TiO_2 (99%) were purchased from Beijing Chemical Works (in China), Nanjing Hydratight Nano Material (China), Xilong Chemical (China), and Tianjin Jinke Fine Chemical Industry Research Institute (in China), respectively. PS (PS-666D) pellets with melt flow index of 8 g (10 min)$^{-1}$ and density of 1.05 g cm^{-3} was purchased from Sinopec Beijing Yanshan Company. Methylene chloride (99.5%) was purchased from Beijing Chemical Works.

Preparation of the BSCT Particles

The synthesis of BSCT particles was followed the procedure as reported.[36] First, stoichiometric quantities of $CaCO_3$, $BaCO_3$, $SrCO_3$, and TiO_2 were mixed in a planetary mill with agate ball and anhydrous alcohol at a rotational speed of 600 rpm for 12 h. Afterwards, the mixtures were dried and sieved (100 mesh). Then the mixtures were calcined at 1100°C for 2 h. The synthesized BSCT powders were placed in a jar mill. After adding appropriate amount of anhydrous ethanol, the mixtures were milled for 4 h and poured into a petri dish, and then dried at 70°C and finally sieved (100 mesh). The density of the powders measured by Archimedes drainage method was about 5.26 g cm^{-3}.

Preparation of the BSCT/PS Composites

A certain amount of BSCT powders and 15 mL methylene chloride were first mixed together in milling tank. After ultrasonic dispersion of the mixture for about 30 min, 2 g PS pellets were added and then mechanically stirred for 1 h. The obtained composite materials were poured in a petri dish and placed in a blast oven to dry for 3 h. Subsequently, the mixture was molded by hot pressing under 15 MPa and at ca. 190°C for 20 min. The achieved samples were cut into discs with area of ca. 1 cm^2 and thickness of ca. 1 mm for the measurements of dielectric properties.

Characterization

X-ray diffraction (XRD) was used to characterize the crystalline phase of BSCT particles using Cu Kα radiation (Rigaku, DMAX-RB). The BSCT particles and cross-section of the BSCT/PS composites were observed by scanning electron microscopy (SEM, S4700, Japan) operating at 20 kV. The samples were fractured in liquid nitrogen before they were observed in SEM. Differential scanning calorimetry (DSC) was measured by Shimadzu instrument DSC-60 (Japan) in a nitrogen atmosphere. The specimens were heated at 10 Kmin^{-1} from 25°C to 150°C. For dielectric measurements, an impedance analyzer (Agilent 4294A) with frequency from 100 Hz to 1 MHz and an RF impedance/material analyzer (Agilent E4991A) with frequency from 1 MHz to 1 GHz were used over a wide temperature range from −30°C to 80°C. For the measurements of dielectric properties, silver electrodes were painted on both sides of the samples before characterization.

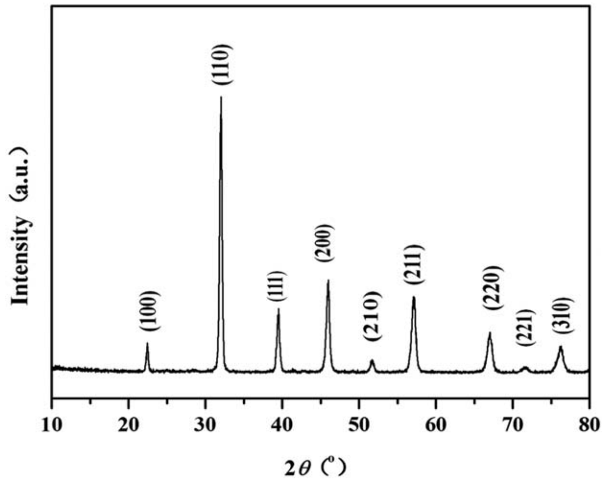

Figure 1. XRD pattern of BSCT particles.

RESULTS AND DISCUSSION

Characterization of BSCT Particles and the BSCT/PS Composites

Figure 1 shows the XRD patterns of the prepared BSCT particles. The BSCT particles show the diffractions corresponding to the (100), (110), (111), (200), (210), (221), and (220) directions. It can be seen that there is a single peak at around 46°, which is a typical XRD pattern of perovskite structure and indicates a cubic structure of BSCT.[7,37] Figure 2 shows the SEM micrographs of BSCT powders and the cross-section of BSCT/PS composites with different BSCT contents. As seen from Figure 2(a), the grain size of the as-prepared BSCT particles was about 1 μm. Most of the particles were in cubic shape and some others possessed irregular shapes. In the composites, the BSCT particles were randomly dispersed in the PS matrix [Figure 2(bd)]. For filler contents up to 50 vol %, there was no serious aggregation observed. With increasing the filler contents, the packing of the BSCT particles grew denser. For the composite with filler content of 64 vol %, there was aggregation of the filler particles and voids among the fillers appeared [Figure 2(e)].

Thermal Properties of Pure PS and the BSCT/PS Composites

Figure 3 shows the DSC curves of pure PS and BSCT/PS composites with various filler contents. A clear glass transition step can be seen at ca. 100°C for the pure PS. With the increase of BSCT fillers, the position of Tg slightly shifted to higher temperature, which indicated a reduced segmental mobility. The step intensity decreased as a result of the reduced fraction of the PS in the composite.

Frequency Dependences of Dielectric Properties of the BSCT/PS Composites

Figure 4 shows the frequency dependence of dielectric constant and dielectric loss of the BSCT/PS composites with various filler contents. The data for the frequency ranged from 100 Hz to 1 MHz were obtained by the impedance analyzer (Agilent 4294A), while the data for the frequency range from 1 MHz to 1 GHz were obtained by the RF impedance/material analyzer (Agilent

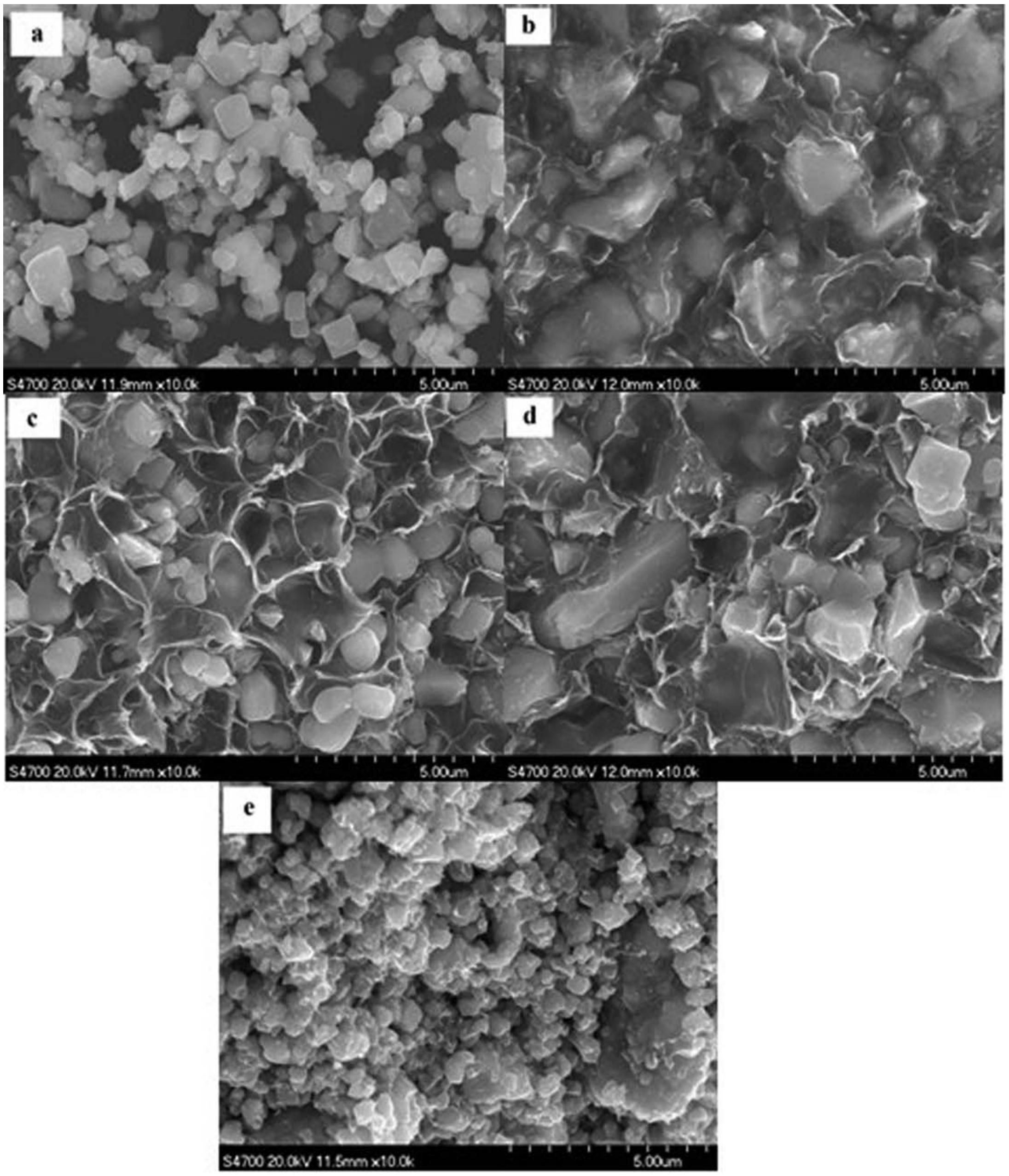

Figure 2. SEM micrographs of (a) BSCT powders and the cross-section of BSCT/PS composites with BSCT contents of (b) 17 vol %, (c) 31 vol %, (d) 50 vol %, and (e) 64 vol %.

E4991A)). According to Figure 4(a), the dielectric constant of the composites increased with increasing filler content as expected, which was because of the high dielectric constant of the BSCT fillers. The dielectric constant of the composites with filler content up to 50 vol % showed good frequency independence at the frequency from 100 Hz to 500 MHz. However, for the composites with filler content of 64 vol %, the dielectric constant decreases sharply with increasing frequency for the frquency below 1 kHz and keeps constant at higher frequency. As well known, the dielectric behavior is derived from the polarization of different structure units such as interface, dipoles, ions, and electrons in the sequence of increasing frequency.[38,39] The rapid decrease of dielectric constant of 50 vol %-BSCT/PS composites at the frequency above 500 MHz may be ascribed to the decreased dipole and electrons polarization. This effect was much less significant for the 17 vol %-BSCT/PS composites. According to Figure 4(b), the dielectric loss of the composites increases with increasing filler content, because of the high dielectric loss of the BSCT fillers. The dielectric loss of all the composites was below 0.03 at the frequency range from 10 kHz to 100 MHz. The dielectric loss increased sharply with decreasing frequency for the frequency below 10 kHz, which might be because of the increasing interfacial polarization and low frequency leak loss.

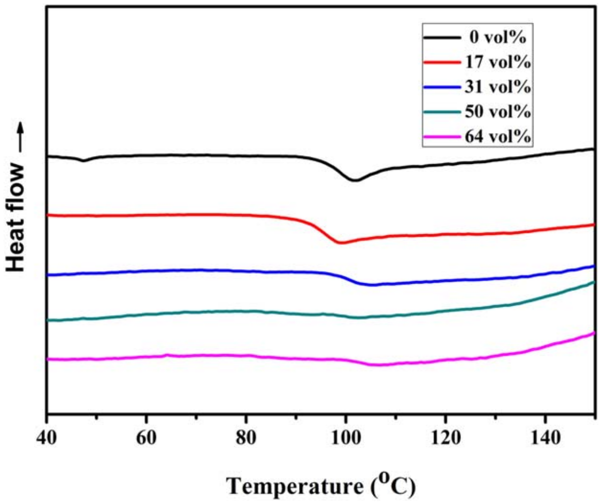

Figure 3. DSC traces of pure PS and BSCT/PS composites with various filler contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

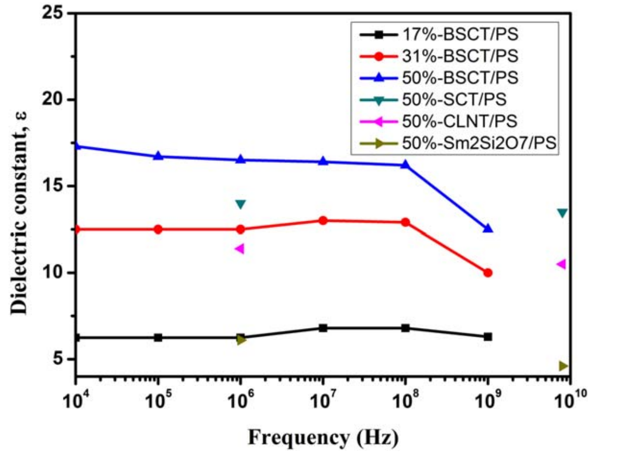

Figure 5. Comparison of dielectric constants between experimental data of BSCT/PS composites and the literature values of $Sm_2Si_2O_7$/PS, SCT/PS, and CLNT/ PS composites with filler content of 50 vol % at room temperature.[40–42] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows the comparison of the dielectric constant of the experimental data of BSCT/PS composites and the literature values of $Sm_2Si_2O_7$/PS, $Sr_2Ce_2Ti_5O_{15}$ (SCT)/PS, and $Ca[(Li_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}]O_{3-\delta}$(CLNT)/PS composites with filler content of 50 vol %.[40–42] It can be seen that at 1 MHz when the filler content was 17 vol %, the dielectric constant of the BSCT/PS composite was already comparable with the 50 vol %-$Sm_2Si_2O_7$/PS composite. And when the filler content reached to 50 vol %, the BSCT/PS composite possessed higher dielectric constant than the reported materials. Although at 1 GHz, the dielectric constant of 31 vol % and 50 vol %-BSCT/PS decreased, it is still comparable with the reported values. In addition, the dielectric loss of the BSCT/PS composite was 0.006 at 100 MHz which was reasonably low. Therefore, considering the general requirements of microwave substrate applications (high dielectric constant and low dielectric loss), the as-prepared BSCT/PS composites could be an appropriate candidate.

Temperature Dependence of Dielectric Constant of the BSCT/PS Composites

Figure 6 shows the temperature dependency of the dielectric constant of BSCT/PS composites with various filler contents at 1 and 100 MHz, respectively. It can be seen that for both frequencies, the dielectric constant increased with increasing filler content and it shows good temperature independence for the temperature range from −30°C to 80°C. Compared to pure PS, the dielectric constants of the 50 vol %-BSCT/PS composite were about 32.2 and 29.7 at 1 and 100 MHz, respectively, in a wide temperature range. These dielectric constants were about 15-time higher than those of pure PS.

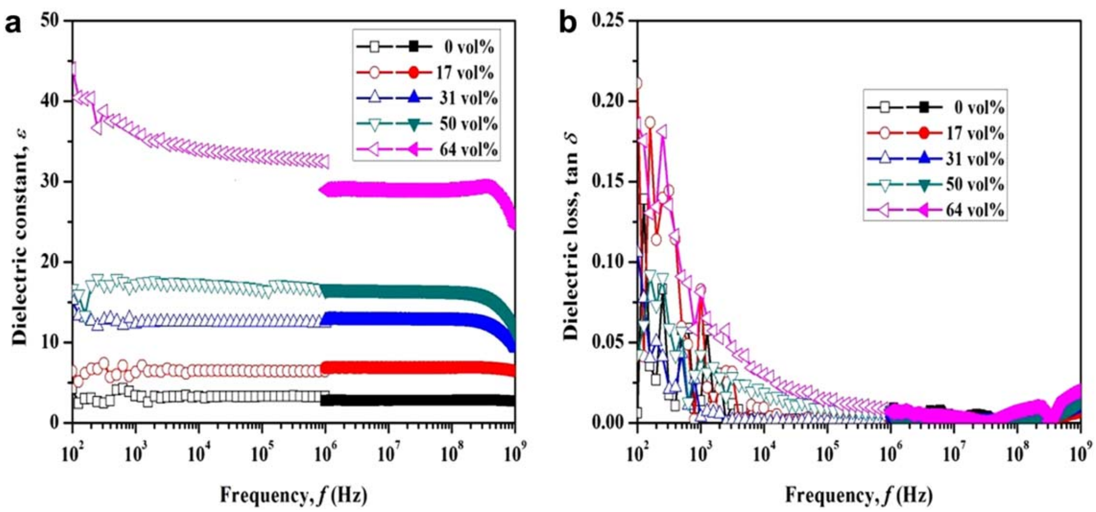

Figure 4. Frequency dependency of (a) dielectric constant and (b) dielectric loss of the BSCT/PS composites with various filler contents at room temperature (The data for the frequency range from 100 Hz to 1 MHz were obtained by the impedance analyzer (Agilent 4294A), while the data for the frequency range from 1 MHz to 1 GHz were obtained by the RF impedance/material analyzer (Agilent E4991A)). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

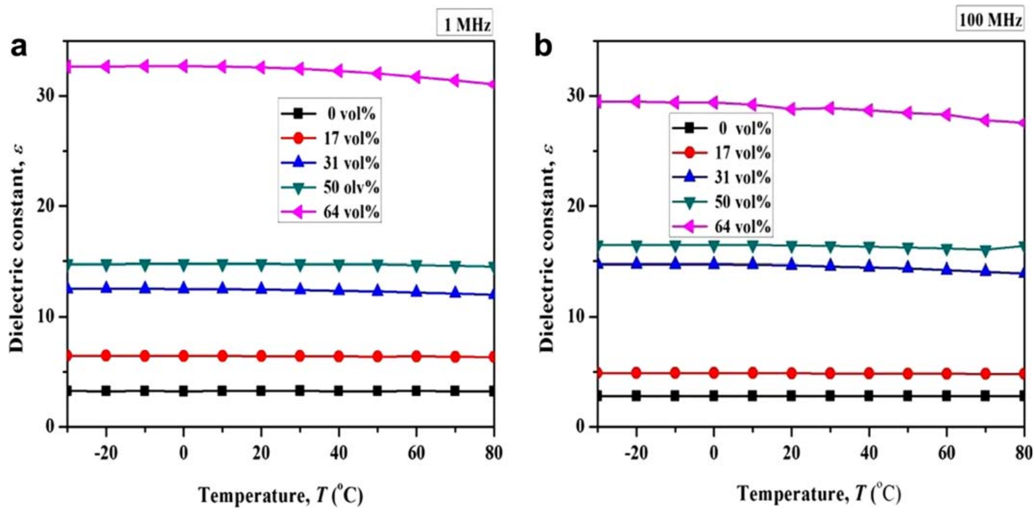

Figure 6. Temperature dependency of dielectric constant of BSCT/PS composites with various contents of fillers at: (a) 1 MHz and (b) 100 MHz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Theoretical Prediction of BSCT/PS Composites

The dielectric constant of the composites can be influenced by the properties of polymer matrix and fillers, content and dispersion of the fillers in the polymer matrix, and their interaction. Several theoretical models that can be used to predict the dielectric constant of polymer composites are as follows[43–45]:

Maxwell–Wagner equation:

$$\varepsilon=\varepsilon_p\frac{2\varepsilon_p+\varepsilon_c+2v_c(\varepsilon_c\text{-}\varepsilon_p)}{2\varepsilon_p+\varepsilon_c\text{-}v_c(\varepsilon_c\text{-}\varepsilon_p)}$$

Lichtenecker equation:

$$\log\varepsilon=v_p\log\varepsilon_p+v_c\log\varepsilon_c$$

Modified Lichtenecker equation:

$$\log\ \varepsilon=v_p\log\ \varepsilon_p+v_c(1-\kappa)\log\left(\frac{\varepsilon_c}{\varepsilon_p}\right)$$

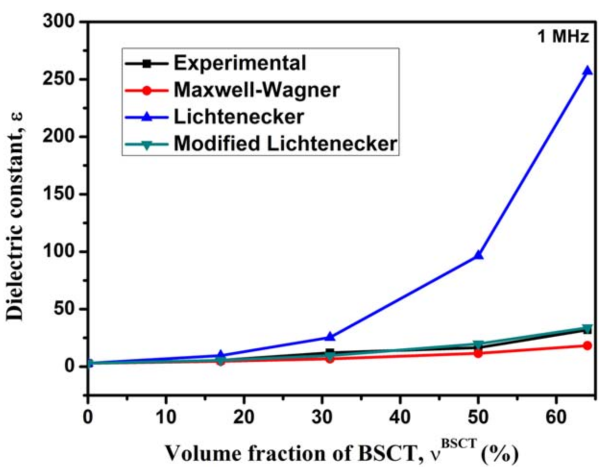

Figure 7. The experimental and theoretical dielectric constant predicted by three models at 1 MHz and room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where ε, ε_p, and ε_c are the dielectric constants of the composites, the polymer matrix, and the fillers, and v_c is the volume fraction of the fillers. k is a fitting constant and has a value of around 0.3 for most well-dispersed polymer composites.

The comparison of the experimental data and theoretical value of the dielectric constant of BSCT/PS composite at 1 MHz is shown in Figure 7. The dielectric constant of the BSCT/PS composites increases with increasing filler content. It can be seen the modified Lichtenecker Equation fits better to the experiment data compared to the Maxwell–Wagner equation and the Lichtenecker Equation. The reason might be that the modified Lichtenecker Equation takes the interphase interaction between the polymer matrix and the fillers in consideration. The Lichtenecker Equation is applicable for spherical fillers which makes it unfit. Maxwell–Wagner equation is for composites with two phases with similar property and low content of fillers. The Maxwell –Wagner equation fits better to the experimental data at low concentrations but diverted at higher loadings.

CONCLUSIONS

Polymer composites with PS as matrix and BSCT as fillers were prepared by solution casting method. The size of the synthesized BSCT was about 1 μm and most of them possessed cubic shape. The dielectric constant of the as-prepared BSCT/PS composites increased with increasing filler content over frequency range from 100 Hz to 500 MHz. The dielectric constant of the composites also showed temperature independency in the range of -30°C to 80°C. For the composite with 50 vol % filler content, the dielectric constant and dielectric loss of the BSCT/PS composite were comparable with the literature values reported for other PS composites used for microwave devices. Theoretical models had been compared with experimental results, and the modified Lichtenecker equation was found to fit the best. The BSCT/PS composites can be considered as a possible candidate for microwave substrate applications.

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