Effect of Dehydroxylation of Hydrothermal Barium Titanate on Dielectric Properties in Polystyrene Composite

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ABSTRACT: In today's world, technology for capacitors has grown significantly with its requirements in the direction of better dielectric properties. Developing an ideal composite material (polymer and ceramic) for satisfying the processing parameters is of great interest for capacitor industry. In this study, chemically treated barium titanate (BT) nanocrystals were prepared and used to make ceramic–polystyrene (PS) composites. A unique methodology was used in processing these materials. Effects of the chemically treated BT, filler loading, and frequency on the dielectric properties of these composites were examined, and compared with untreated BT–PS composites. Composite dielectric constant was proportional to the volume ratio of the BT filler and remained stable at different frequencies. The experimental data show that the dielectric constant of composites made with treated BT powders can attain values 2.5 times higher than that of untreated BT–PS composites. In addition, the composite shows consistency in dielectric constant values measured at different frequencies. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2815–2821, 2006

Key words: polystyrene; barium titanate; composite

INTRODUCTION

Recently, the focus of research has been on the use of polymer–ceramic composites in embedded capacitor technology. On filling a polymer matrix with ceramic particles, the resulting composite exhibits different electrical characteristics. When nonconductive ceramic filler with high permittivity, *e.g.* barium titanate (BaTiO$_3$; BT), is used, then one can control the dielectric properties of the composite by changing the filler content. From the time when electronic devices using ferroelectric ceramics, such as multilayer capacitors, have been miniaturized, effects of particle size on the physical properties have become very important. There have already been several reports on particle size effects in BT ceramics as well as in BT–polymer composites.[1–9] Novel methods to produce particles that are finer in size and homogeneous in composition are some of the key factors. This alone has important implications to embedded ceramic capacitor applications.

Embedded decoupling capacitors show better electric performance because they are placed closely to the chips, resulting in reduced parasitic inductance. Important requirements for embedded capacitor materials are high dielectric constant, low capacitance tolerance, good processability, and low cost. However, no single material can meet all these requirements. For example, thin film capacitor materials formed by vacuum deposition have the advantage of fairly high capacitance, while they have the drawbacks of high processing temperature and cost.[10]

In bulk BT ceramics, grain size has a strong effect on the dielectric constant at room temperature for the grain size below ~10 μm.[2,11] Dielectric constant increases with decreasing grain sizes up to a maximum of ~700 nm.[10] Below this size, dielectric constant sharply decreases, in conjunction with the reduction of tetragonality and remnant polarization.[10] The crystal structure of BT powder changes with particle size. Below ~100 nm, tetragonality disappears, resulting in a cubic structure. Therefore, it can be expected that the dielectric constant of BT powder will vary with BT particle size.

Polymer–ceramic composite, with polymer as the matrix, is one of the promising materials for embedded capacitor.[12–14] It utilizes the high dielectric constant of ceramic powders and good processability of polymers, resulting in lower processing temperature and cost.[10] It has been reported that for ceramic–polymer composites, epoxy is a suitable polymer for its inertness to the electroless plating solution and its compatibility with printed wiring boards. BT has a high dielectric constant of ~6000 at a fine grain size of 1 μm.[1,2] Different types of treatment have been applied to the dielectric BT to move the Curie peak value toward room temperature to improve the capacitance, and to smooth the Curie peak to have lower temperature coefficient of capacitance. These treatments can

either decrease or increase the Curie point and change the dielectric constant as required. For ceramic–polymer composites, BT is in the unsintered powder form. As compared with sintered BT, unsintered BT powder can show difference in dielectric behavior.[15]

The dielectric constant of the ceramic used in the composite is one of the most important factors for determining the composite dielectric constant as well as the volume fraction of ceramic particles required for the composite. Recent improvements in achieving even higher dielectric constants are based on the normal particle distribution of treated ceramic particles that have tetragonal structure. Few studies have so far been focused on polystyrene (PS)–BT composites. It has been reported that the nanocrystalline BT and polymer PS sodium sulfonate were used to form composite material in fabrication for humidity sensors.[16] Until now, BT and PS composites were not studied for their dielectric properties. In this study, we have examined dielectric properties of BT–PS composites as a function of BT content in polymer. The object of this work was to produce dense BT–PS composites with high dielectric constant and low loss factors. The nanocrystalline cubic BT used in this work was treated chemically with dimethyl formamide (DMF) to enhance the tetragonality of BT. Dry pellets were made by using different volume percentages of BT in PS. A special type of methodology was used to obtain high density BT–PS pellets. Dielectric properties were then explained with respect to ceramic loading content and frequencies and compared with untreated BT–PS composites. By optimizing this process, a ceramic–polymer composite with a high dielectric constant has been obtained.

Homogeneous dispersion of ceramic nanocrystals in a polymer matrix is an issue of both scientific and technological interest. The structure–property relationship in a composite has been a subject of extensive scientific investigation.[17,18] Because of the unique properties and processing flexibility of composites, which in many cases cannot be obtained from their components, these materials have found numerous technological applications.[19] In general, the electrical properties of composites having less than 60 vol % ceramics have been widely studied. Simple analytical equations predict that high dielectric constant composites may be obtained by increasing the ceramic content in the polymer matrix. However, for composites greater than 60 vol % ceramics, there are a number of processing factors that can influence the dielectric properties of material.[20]

EXPERIMENTAL

The chemical treatment of BT

Initially, 2 g of commercial cubic phase BT powder (Cabot, BT-08) of mean particle size 240 nm was dis-

TABLE I
Specification of BT Powder[a] Used in This Study

Powder	BT-8
Manufacturer	Cabot Corp.
Diameter	240 (nm)
Density	5.9 (g/cc)
Specific surface area	8.5 (m^2/g)
Ba/Ti ratio	~1.000

[a] Supplied by the manufacturer.

persed in 75 mL of DMF in an autoclave. Materials specification of highly pure commercial hydrothermal BT powder (Cabot, BT-08) is shown in Table I. The reaction was carried out in a 100-mL Teflon-lined stainless steel autoclave (Parr Instrument Co.) without any agitation. The autoclave was heated to 170 and 200°C for 6 h in an oven. After cooling down to room temperature in the oven, the resultant precipitate was centrifuged and washed with a mixture of water/alcohol several times, and finally dried at 80°C for 24 h in a vacuum oven. Series of BT samples were prepared for use in the synthesis of composites. We have examined the phase transformation in BT powders from metastable cubic to ferroelectric tetragonal phase.[21] Scanning electron microscope (SEM) images of as-received and chemically treated BT powder are shown in Figure 1. Crystal structures of treated and untreated BT powders were investigated by room temperature X-ray diffraction (RTXRD; Scintag PAD V using Cu Kα line with λ = 0.15406 nm) with step scan mode: step size 0.02°, 5 s/step, 2θ = 20−80° at 40 kV and 40 mA.

The processing of BT–PS composites

BT was chosen as ceramic filler. Specially formulated PS obtained from Aldrich Chemicals was used as the polymer matrix. Fabrication procedure of BT–PS composite is shown in Figure 2. First, PS was dissolved in ~15 mL of toluene in a glass vial with the help of a magnetic stirrer for 8 h. After that, BT nanocrystals were added to the mixture and stirred for 12 h to get a well-dispersed slurry. The slurry was dried in a vacuum oven at 60°C for 24 h. BT loadings of 20, 40, 50, 60 and 80 vol % in BT–PS composites were prepared.

Composite fabrication technique

Dry pellets of BT–PS composites were prepared by using BT–PS powder samples compressed and heated to 140°C in a mold at a rate of 10°C/min. To form the pellet, 42.5 MPa of pressure was applied three times for 1 min each, and then the pressure was held constant at 10 MPa until the temperature reaches 140°C to
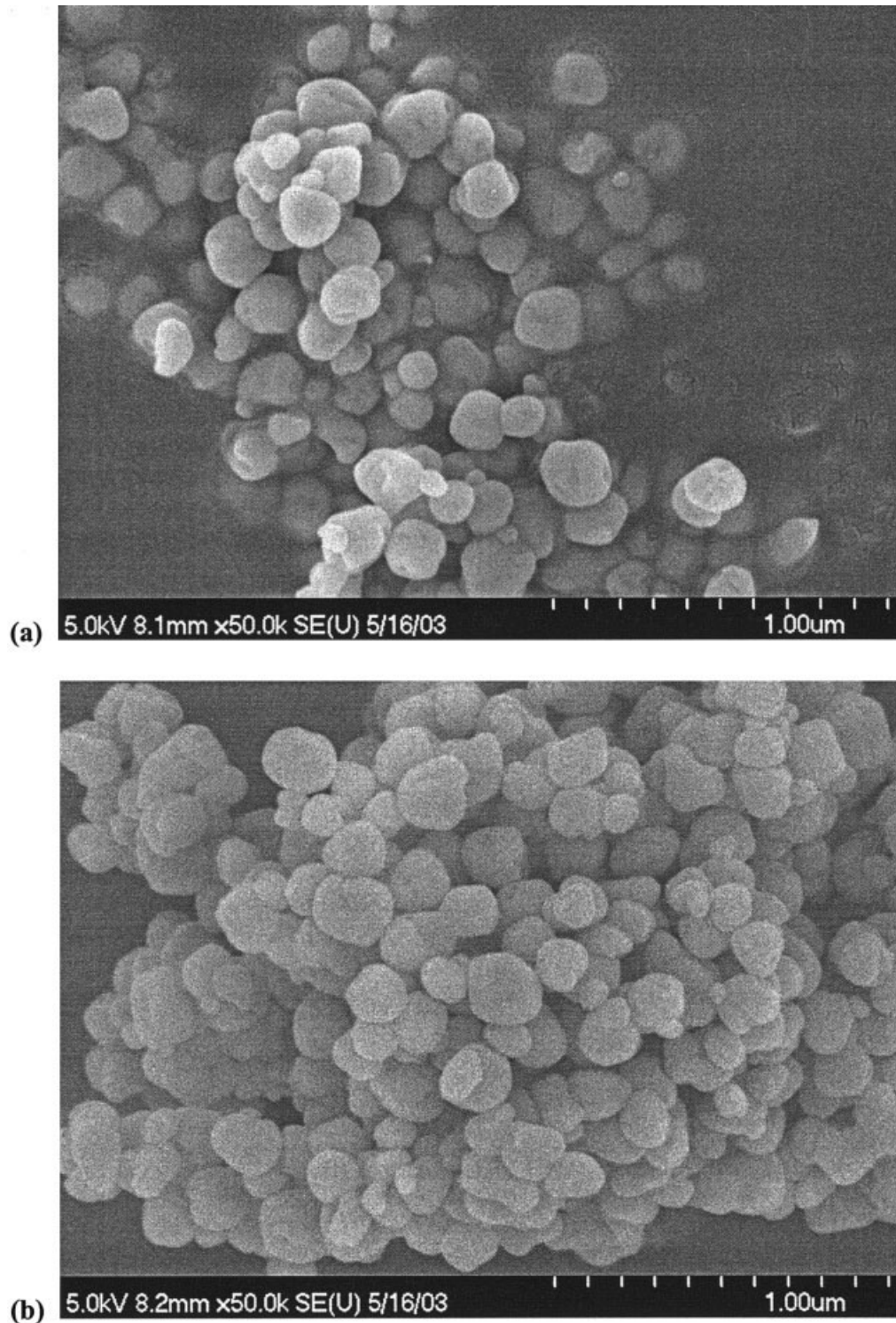
Figure 1 (a) SEM image of as-received BT particles and (b) SEM image of treated BT particles at 170°C for 24 h.

ensure good compactness of the resultant composite specimens. After 15 min, the compressed specimen was then cooled in the mold to room temperature, ~25°C. The resultant pellets, measuring 10 mm in diameter and 2 mm in thickness, were used for further property measurements and characterizations.

Property measurements

Density measurements

The pellets were polished to obtain flat surfaces and relative densities were measured geometrically using the linear combination of matrix and filler.
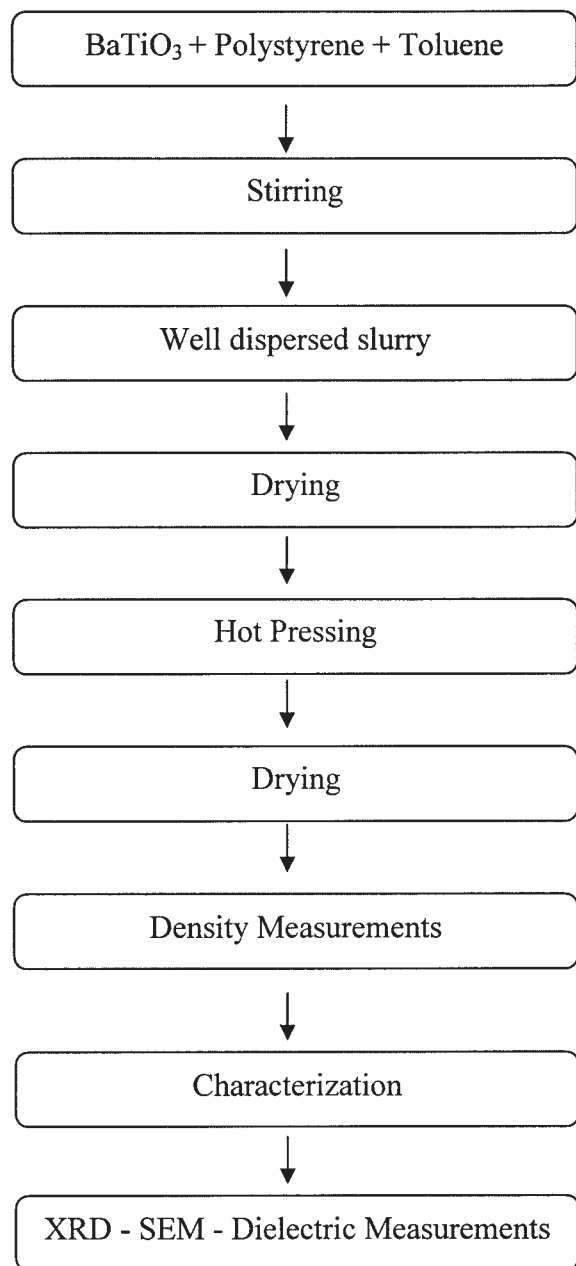
Figure 2 A flow chart showing preparation of the BT–PS composites.

Impedance measurements and analysis

Prior to dielectric constant measurements, the surfaces were coated with silver electrodes and cured in vacuum dryer at 50°C for 2 h. A HP 4284A Precision LCR meter (Hewlett–Packard, USA) connected to a probe station was used to measure the capacitance and dissipation factor. All the samples were subjected to tests at a set time to eliminate the changes in dielectric response over time. Several pellets were measured, and an average of the dielectric constant (ε_r) and dissipation factor values in the frequency range of 20 Hz to 1 MHz at room temperature were recorded. The

dielectric constant of the composite was calculated using this formula:

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A}$$

where, C is the capacitance value of the pellet, A is the area of electrode applied, d is the thickness of dielectric layer, and ε_o is the permittivity of free space (8.854 $\times 10^{-12}$ F/m). The measurements were averaged over three or more pellets to obtain the average dielectric constant values.

Characterization

RTXRD (Scintag PAD V using Cu K_α with $\lambda = 0.15406$ nm) was used for crystalline phase identification of the powder samples (step scan mode: step 0.02°, 5 s/step, $2\theta = 20-80°$ at 40 kV and 40 mA). SEM studies were conducted on these pellets prepared from different ceramic–polymer contents to understand the effect of process deviation on the final particle packing of the composites.

RESULTS AND DISCUSSION

A common problem associated with the inorganic–organic composites is the incompatibility of the two materials resulting in structural inhomogeniety.[22,23] In the system of BT–PS, the surfaces of BT with hydroxyl groups are highly polar and hydrophilic in nature, while the PS and organic solvent are nonpolar and hydrophobic. When these different materials are mixed, the BT particles tend to segregate and agglomerate, thus resulting in processing difficulties with an inhomogeneous distribution of BT particles in the polymer. The removal of hydroxyl groups on the surface of BT by chemical treatment is believed to improve the dispersion of BT in PS resulting in composites having a uniform microstructure.

Figure 3 shows the XRD patterns of the three BT powders: untreated Cubic BT, DMF-treated tetragonal BT, and DMF-treated BT–PS. The positions of XRD peaks of DMF-treated tetragonal BT are similar to those of untreated cubic BT, but the tetragonal structure can be discriminated from the cubic structure by observing peak splitting at 45° 2θ angle. This region of the diffraction pattern is characteristic of the tetragonal form of BT.[24] There is a splitting of the (200) reflection in the tetragonal form, with the lower angle shoulder indexed as (002).[25] Based on these results, it is apparent from Figure 3 that the BT treated with DMF in the tetragonal form would show higher dielectric constant in BT–PS composite as compared with untreated cubic BT. The XRD patterns for DMF-
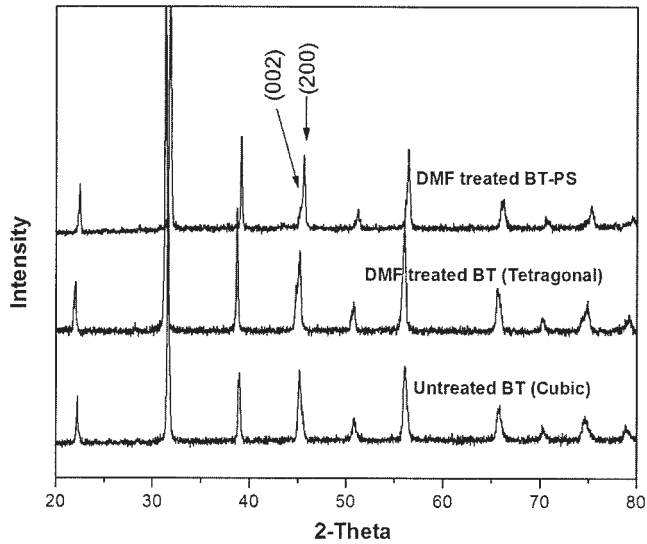
Figure 3 XRD patterns of untreated BT, DMF-treated BT, and DMF-treated BT–PS.

Figure 5 Dielectric constant of BT–PS composites.

treated BT–PS composite showed no detectable secondary phase induced in the material.

Figure 4 shows a variation of the relative density, as the volume fraction of BT increased in PS. A solid loading of 40 vol % BT is found to be optimum for high relative density. The values of the relative densities obtained for the untreated and treated 40% BT–PS composites are of the order of 99.8 g/cc. A gradual decrease in relative density is observed with an increase in ceramic content of more than 50 vol %.

The dielectric properties of untreated BT–PS composites having different volume percent of BT at different frequencies are shown in Figure 5. As the volume percent of BT increases, the dielectric constant (k) of the composite increases as expected with respect to
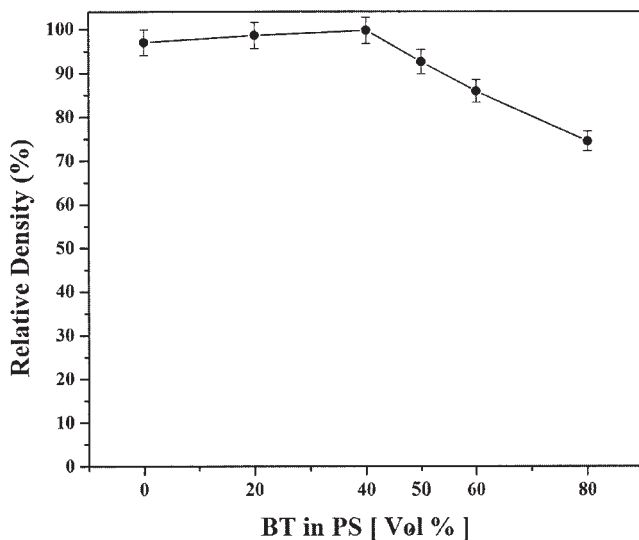
higher ceramic filler in the composite. The dielectric constant at 40 vol % loading of BT gives consistent results at different frequencies when compared with higher BT loading in the composites. Figure 6 shows that the dielectric loss decreases at different frequencies, as the BT content in the untreated BT–PS composite decreases. Dielectric loss of 40 vol % BT composites is 0.013 at 1 MHz. Figure 7(a) shows the SEM of the composite surface 40 vol % BT in the PS matrix.

The dielectric constants of untreated BT–PS, DMF-treated (170°C/6 h) BT–PS, and DMF-treated (200°C/6 h) BT–PS composites at [40–60 vol %] of PS at different frequencies are given in Figure 8. It was observed that the dielectric constant of the composite increased as high as 70 at 1 kHz and 40 at 1 MHz frequency
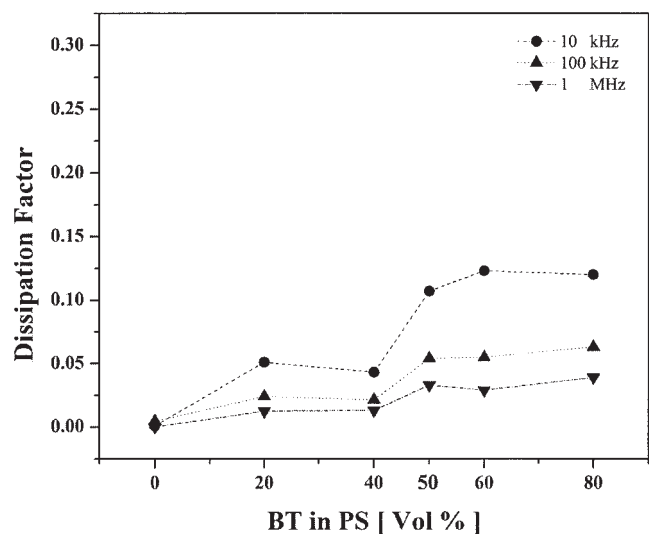

Figure 4 Relative Density of untreated BT–PS composites.

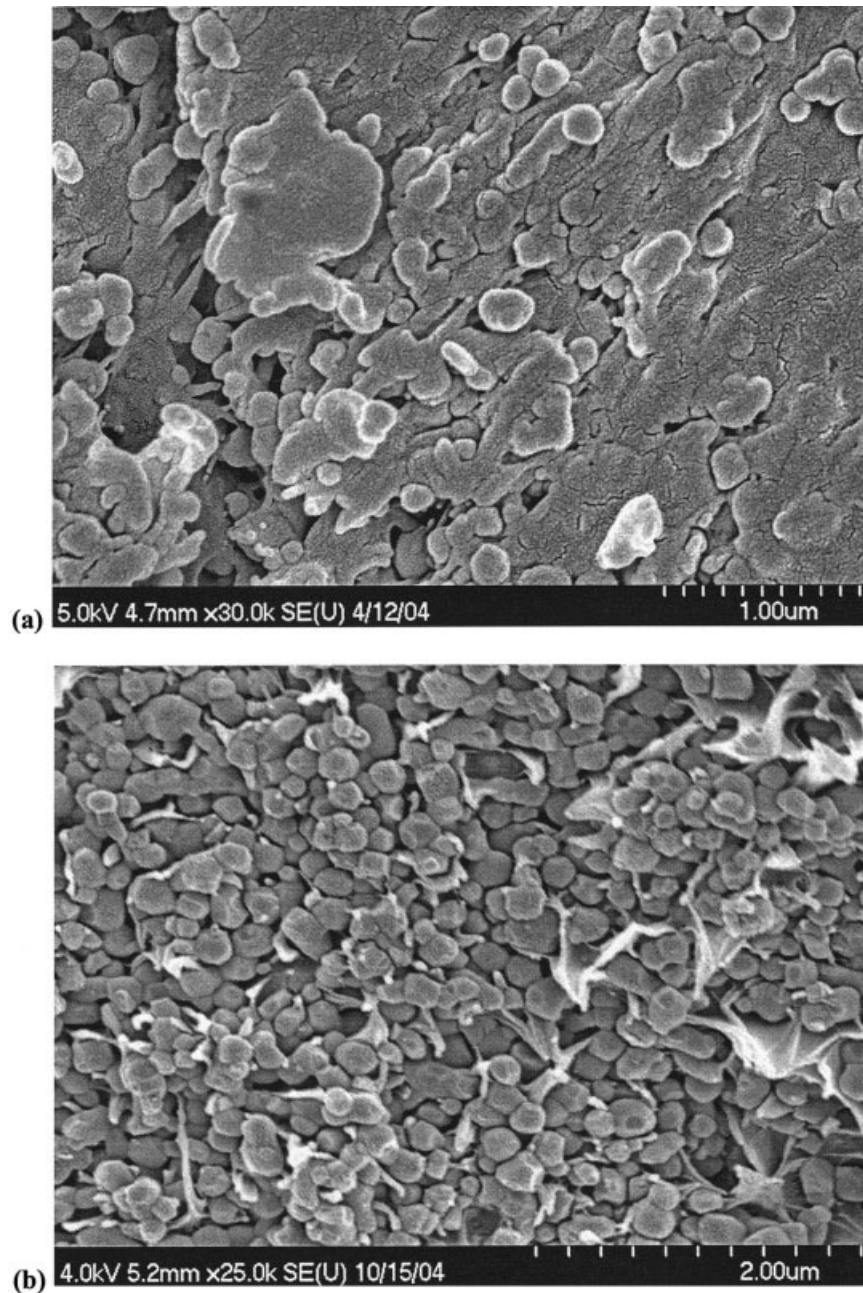**Figure 6** Dielectric loss of untreated BT–PS composites.

Figure 7 (a) SEM image of untreated BT–PS [40–60 vol %] and (b) SEM image of DMF-treated BT–PS [40–60 vol %].

range. The DMF-treated samples show higher dielectric constant values when compared with untreated samples. The reason being, chemically treated BT powders have gone through surface modification and structural change from cubic to tetragonal, resulting in higher dielectric constants of composites. This increase can also be attributed to the uniform dispersion of the BT powder in the PS matrix and the enhanced polarization from the dipole–dipole interaction of closely packed powders, as compared with untreated BT–PS composites. Figure 7(b) shows the surface of 40 vol % BT in the PS matrix, which indicates a better distribution of the PS.

CONCLUSIONS

The distinctive ceramic/PS composites, having BT as ceramic filler, were investigated and discussed in this article. In terms of the materials formulation, these composites are composed of commercially available cubic BT-08, which was chemically treated with DMF and research grade PS. In terms of composite technique, a unique methodology was used to produce high density pellets of BT–PS with different ceramic loadings to analyze their dielectric properties. A composite with 40BT–60PS exhibited good consistency in dielectric constant values in the frequency range of 1
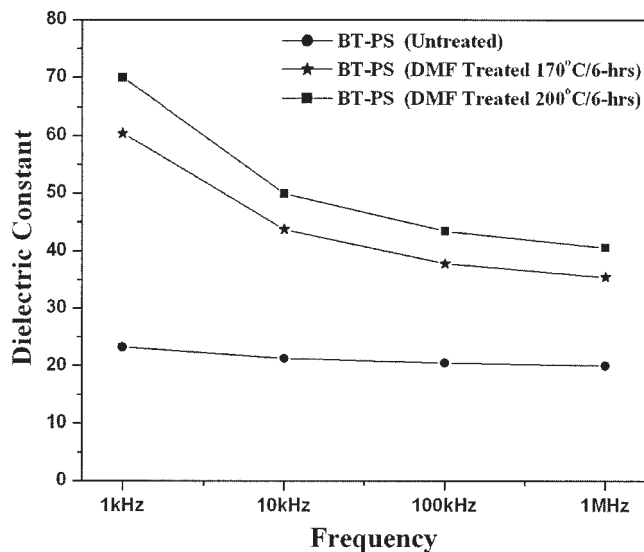
Figure 8 Dielectric constant of untreated BT–PS, DMF-treated (170°C/6 h) BT–PS, and DMF-treated (200°C/6 h) BT–PS composites at [40–60 vol %].

kHz to 1 MHz with relative density of about ~99.98%. A maximum dielectric constant of 70 at 1 kHz with a composite of 40BT–60PS was obtained with the DMF-treated BT powder, a value ~3 times higher than the one obtained for untreated samples. At higher frequencies, the dielectric constant drops gradually but is still 2 times higher than that of values observed in untreated powders. These results clearly demonstrate the improvement in the dielectric properties of the powder, which, if used in making films, may meet the high capacitance density requirements of the film capacitors.

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