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RF properties of BST–PPS composites

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Abstract

Ferroelectric ceramic–polymer composites provide flexible self-sustaining thin layers with unique electrical and mechanical properties, and thus a novel way to fabricate RF devices. In this work, a composite made of ferroelectric ceramic (barium strontium titanate, BST) and thermoplastic polymer (polyphenylene sulfide, PPS) was studied with various BST loadings up to 70 wt.%. The microstructures exhibited uniform distribution of ceramic particles in the polymer matrix. RF measurements showed that the relative permittivity and loss tangent of the composites gradually increase with increasing BST loading. At 1 GHz a composite with 70 wt.% BST loading had relative permittivity and a loss tangent of 13.5 and 0.0025, respectively.

Keywords: Extrusion; Composites; Microstructure; Dielectric properties; BST–PPS

1. Introduction

Ferroelectric ceramic–polymer composites for microelectronics devices have been an important application area in recent years.[1,2] These materials are good candidates for embedded capacitors, capacitively coupled electrical solutions and other integrated high-frequency electronic devices in multilayered structure. Ferroelectric ceramic–polymer composites made of barium strontium titanates $Ba_{1-x}Sr_xTiO_3$ (BST) with different polymers, such as epoxy, polyvinylidene fluoride (PVDF), polyimide, cyanoethylated cellulose polymer, etc., have been investigated.[3–9] BST is a versatile ferroelectric compound for capacitors and high frequency devices due to its good electrical properties and low cost.[10,11] Strontium decreases the Curie temperature of ferroelectrics and thus, for example, $Ba_{0.55}Sr_{0.45}TiO_3$ is in a paraelectric state at room temperature. However, the dielectric loss ($\tan\delta$) of BST ceramic is relatively high for RF devices operating in the GHz frequency range. Additionally, the brittleness and rigidity of the ceramic limit its utilization in miniaturized multilayer structures. On the other hand, polymers are low-cost materials with good thermal property, chemical stability, mechanical strength, and flexibility, and they can be easily processed even into complex shapes. In addition, some polymers have a very low loss tangent, and especially thermoplastic polymers have good thermal properties matching with the processing requirements of multilayer RF structures. Up to now, only a few studies of ferroelectric ceramic and thermoplastic polymer composites have been made.[12,13]

In this work polyphenylene sulfide (PPS) was chosen as a polymer matrix because it is a semicrystalline thermoplastic polymer offering well-balanced characteristics like good flowability, dimensional stability, electrical properties, and high temperature and chemical resistance. It has therefore already been used in commercially available film capacitors. In our experiments, PPS was chosen especially because of its very low dielectric loss at high frequencies. Studies of composites made of PPS and Al_2O_3, SiC, Si_3N_4, and Cr_3C_2 ceramic fillers[12] have been reported. More recently, research has been conducted on PPS and nano-oxide particles of TiO_2, ZnO, CuO, and SiC[13] to enhance their wear and tribological behaviors.

In this work the main purpose was to study the high frequency properties of BST–PPS composites for wireless telecommunication applications. Samples were fabricated by extrusion with various BST loadings, and their dielectric properties (ε_r and $\tan\delta$) were measured with an impedance analyzer at high frequencies (10 MHz to 1 GHz). The concentration dependence of the dielectric properties of BST–PPS composites was studied and their microstructures were analyzed with a scanning electron microscope.

2. Experimental

The composites were fabricated using a HAAKE PolyLab OS system with a PTW16 twin-screw extruder (Ø16 mm, L/Ø

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of 25) (Thermo Electron GmbH, Germany). The PPS (FORTRAN 9205C4, density 1.35 g/cm^3) was provided by Ticona Norden Finland Oy. BST powder with an average particle size of ~1 μm ($Ba_{0.55}Sr_{0.45}TiO_3$ calcined at 1100 °C for 4 h, density 5.50 g/cm^3) was provided by Filtronic Comtek Ltd., UK. The extrusion proceeded through different zones with a screw speed of 200 rpm. The melting temperature of PPS is 280 °C, thus an extrusion temperature of 300–310 °C was used. The granular PPS polymer was fed in zone 1 by a standard volumetric single-screw metering feeder at room temperature. The temperature of zone 2 was 310 °C. The BST powders were fed into the molten PPS by a gravimetric twin-screw feeder, and they were compounded in zone 3 at 310–320 °C. After compounding, sheet samples 20–30 mm wide and 0.2–0.3 mm thick were extruded through the die (290 °C). In order to obtain a suitable sample size (30 mm × 30 mm × 1 mm) for measurements, the sheets were cut into small pieces and hot-pressed with a mold.

The BST loading of the composites was determined from the feeding speed of BST and PPS. For example, when PPS was fed at a speed of 300 g/h and BST powder at 700 g/h, BST loading was 70 wt.% and the volume fraction was 36.4 vol.%, calculated using the density values of pure PPS and BST. The microstructures were studied with a Jeol JSM-6400 scanning electron microscope (SEM, Jeol Ltd., Japan). The specific surface area of the powder was measured with a COULTER OMNISORP 360CX (Coulter Electronics Ltd., UK). The crystal phase of the BST in the composition was studied with a Siemens D5000 X-ray diffraction spectrometer (XRD, Siemens AG, Germany). The relative permittivity and loss tangent of the BST–PPS composites were measured with an Agilent E4991A RF Impedance/Material Analyzer (Agilent Technologies Inc., USA) in a frequency range of 10 MHz to 1 GHz.

3. Results and discussions

Five different loadings of BST–PPS compositions were prepared from BST powder and granular PPS. The specific surface area of the calcined BST powder was 7.8 m^2/g, and XRD analysis showed that it has a barium strontium titanate polycrystal structure, as expected. After sintering at 1400 °C for 4 h, the bulk BST had a density of 5.5 g/cm^3, ε_r of 1757, and tan δ of 0.001 at room temperature at 100 kHz.

The BST loadings of composites 1C, 2C, 3C, 4C and 5C were 30, 42, 50, 60 and 70 wt.%, respectively. The SEM images (in back-scattering electron mode) of the samples (Fig. 1) show the very dense and homogeneous microstructure of the BST–PPS composites. Thus, the mixing process and parameters used for composite manufacturing are adequate, and uniform measurement results as well as good correspondence with theoretical models can be expected. The BST filler with a particle size of ~1 μm and a narrow size distribution can be seen in Fig. 1. The BST–PPS composites had almost no void in their microstructures, which is one advantage compared to bulk ceramic, where voids remain in the microstructure after sintering.[11]

The relative permittivity and loss tangent values measured with an impedance analyzer for composites 1C and 5C are shown in Fig. 2, while the other composites, 2C–4C, exhibit similar behavior. The data had some variation in the lower frequency range (<20 MHz) due to the limitation of the impedance analyzer system. The relative permittivity values of the composites stay nearly the same in the frequency range of 10 MHz to 1 GHz, with a slight increase as the frequency increases, as shown in Fig. 2. The ε_r changes were in the range of 0.6–2.2%, and higher BST loading increased the changes. The loss values remained almost constant, but they increased slightly at higher frequencies, which is a common trend in dielectric ceramics.

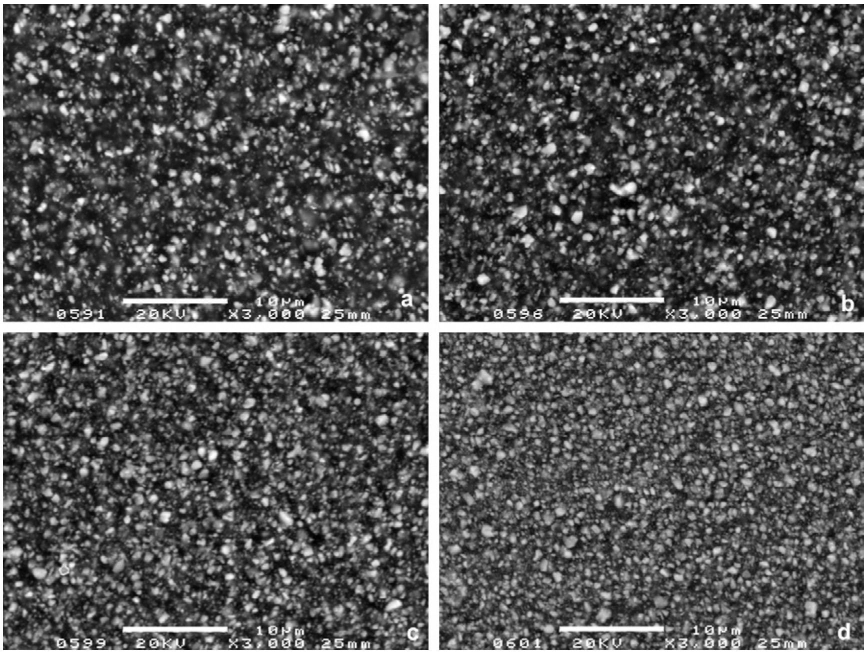

Fig. 1. SEM images of BST–PPS composites (a) 2C, (b) 3C, (c) 4C and (d) 5C.

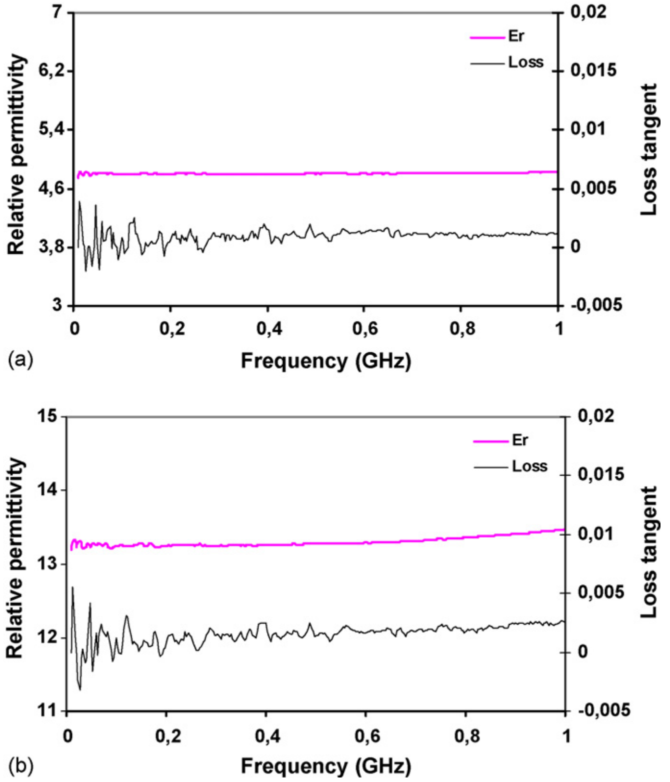

Fig. 2. Impedance analyzer results for (a) 1C and (b) 5C BST–PPS composites.

The average values of relative permittivity and loss at 0.97–1 GHz are listed in Table 1. According to the manufacturer's information, the relative permittivity of pure PPS is 3.2 at 1 MHz. The same value of relative permittivity and a loss tangent of 0.001 was obtained for pure PPS with an impedance analyzer at 1 GHz. The relative permittivity of the BST–PPS composites at 1 GHz increased from 4.8 to 13.5 while BST loading increased from 30 to 70 wt.%. Correspondingly, the loss tangent increased from 0.0012 to 0.0025, as shown in Table 1, but stayed within a feasible range for utilization in high frequency solutions.

Relative permittivity and loss as a function of BST loading at 1 GHz is shown in Fig. 3. As mentioned earlier, the relative permittivity of the composites gradually increased as a function of BST loading. Several dielectric mixing models have been proposed and investigated, such as series, parallel, Hashing-Shtrikman and Lichtenecker models,[5] a numerical model based on Monte Carlo simulations,[14] and an effective-medium theory.[15] The most commonly used model for a well-dispersed ceramic–polymer composite is the Lichtenecker model. The relative permittivity ε of the composites followed the log–law relationship:

Table 1
Relative permittivity and loss tangent of the composites measured with an impedance analyzer

Number	BST (vol.%)	BST (wt.%)	Relative permittivity at 1 GHz	Loss tangent at 1 GHz
1C	9.5	30	4.82	0.0012
2C	15.1	42	5.44	0.0013
3C	19.7	50	6.96	0.0016
4C	26.9	60	9.04	0.0014
5C	36.4	70	13.46	0.0025

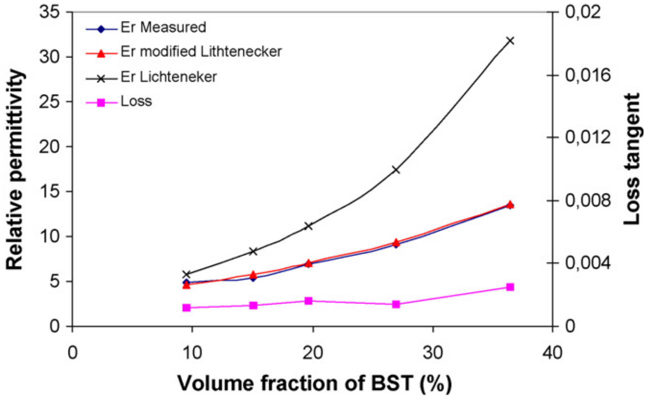

Fig. 3. Mixing models, measured relative permittivity and loss as a function of BST loading at 1 GHz.

$$\log\ \varepsilon = \upsilon_{\mathrm{p}}\ \log\ \varepsilon_{\mathrm{p}} + \upsilon_{\mathrm{b}}\ \log\ \varepsilon_{\mathrm{b}}$$

The following modified Lichtenecker equation[15] was also used:

$$\log\ \varepsilon = \log\ \varepsilon_{\mathrm{p}} + \upsilon_{\mathrm{b}}(1-k)\log\left(\frac{\varepsilon_{\mathrm{b}}}{\varepsilon_{\mathrm{p}}}\right)$$

where k is a fitting constant subject of composite, ν_{p} and ν_{b} are the volume fractions of the polymer and ceramics, and ε_{p} and ε_{b} are the relative permittivities of the polymer and ceramics, respectively. It is reported that $k = 0.3$ for the most well-dispersed polymer–ceramic composites,[15] and for our BST–PPS composites $k = 0.37$ was used, which was determined by matching the model and measurements. The calculated relative permittivity values using the Lichtenecker and modified Lichtenecker equations are plotted in Fig. 3. Good correspondence was obtained with the modified Lichtenecker equation.

4. Conclusions

Novel BST–PPS composites were fabricated from thermoplastic polymer by extrusion, and their dielectric properties were studied in a frequency range of 10 MHz to 1 GHz. The relative permittivity and loss tangent of the BST–PPS composites depend on the ceramic loading of the composites. The research showed that the relative permittivity of the composites gradually increases as a function of BST volume fraction. The dielectric loss behavior of the composites was the same, however, and the loss tangent remained quite low (<0.003 at 1 GHz), which is a promising characteristic for multilayer devices in the GHz range. Generally, the behavior of the composites was well in line with earlier studies with different materials. As a consequence, good correspondence in relative permittivity values was obtained with the modified Lichtenecker equation.

BST–PPS composites showed promising high frequency electrical characteristics in addition to their good formability due to the thermoplastic polymer PPS. They can be easily fabricated as large thick-film dielectrics using a hot-pressing method, for example. Higher permittivity using higher BST loading is expected in the future.

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