

## ORGANIC-INORGANIC RF COMPOSITES WITH ENHANCED PERMITTIVITY BY NANOPARTICLE ADDITIONS

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**Abstract**—Organic-inorganic thermoplastic composites offer a cost-effective material choice with tuneable dielectric properties for various telecom components and applications. Typically such composites require substantial loading of inorganics to obtain a feasible level of permittivity at RF frequencies dramatically decreasing mechanical ruggedness and increasing losses. In this paper we demonstrate utilization of nanoparticle phase in BaSrTiO<sub>3</sub>-polypropylene-graft-poly(styrene-stat-divenylbenzene) composite to enhance the high frequency properties and overcome the problems associated with high filler loading. The effect of nanosize silicon, silver and Al<sub>2</sub>O<sub>3</sub> additives with different volume fractions in complex permittivity was investigated up to 1 GHz. Significant increase in the effective permittivity of the composites with all the additives was observed, especially in the case of the nanosized silver particles where only 2 vol.% addition was able to enhance  $\epsilon_r$  by 52% without increasing the dielectric losses when compared to the reference sample.

### 1. INTRODUCTION

By combining high permittivity ceramic or metal powders with the superior processability and ductility of the polymers, organic-inorganic composites with high effective permittivity and breakdown strength can be developed. Such composites, especially with low loss in the GHz region, are good candidates to fulfil the requirements of the electronic and telecommunication industry for embedded capacitors, capacitively coupled electrical solutions, antenna substrates and integrated RF devices for example. Thus they have been widely studied during recent

years, especially 0-3 type composites that have gained special attention due to their easy and industrially viable fabrication methods [1–4]. Recently, BST-PPS, SrTiO<sub>3</sub>-POE and BZN-PTFE composites have been developed for microwave applications having micron size ceramic inclusions in a polymer host [5–9]. In 0-3 type composites, the effective dielectric properties are dominated by the matrix material thus in ceramic-polymer composites, the net permittivity is greatly reduced from the sintered bulk ceramics due to the significantly lower permittivity of the polymer. Permittivity of the composite is adjusted by inducing sufficient volume fraction of inorganic filler. Typically a high fractional amount of inorganic is required to obtain a significant increase in permittivity thus reducing drastically the processability and mechanical ruggedness of the material [1, 5–9]. Obtaining high effective permittivity and low losses is especially challenging at high frequencies due additional decrement of the permittivity as a function of frequency caused by dielectric relaxation [10–12]. Very high dielectric constants have been experimented at low frequencies with Ni-PVDF composites ( $\epsilon_r \sim 400$ ,  $\tan \delta > 0.15$  at 100 Hz) [13].

To overcome the aforementioned problems conductive, semiconductive or dielectric nanosize filler materials can be used. In such cases the controlled dispersion together with cost-effective processing of nanocomposites becomes an issue as the nanoparticles tend to agglomerate, thus negating the possible benefits obtained from the nanoscale dimensions [1]. However, a slight increase of relative permittivity has already been reported by utilising BST nanoparticles and industrially viable manufacturing methods, although still exhibiting greatly increased dielectric losses at 1 GHz [14]. More recently, a small amount of silver has been used to enhance the dielectric properties of the ceramic-metal composites [15].

In this work, we present an injection mouldable thermoplastic ceramic-polymer composite with improved dielectric properties by utilising third material phase of nanosize inclusions. Measurement data of the complex permittivity of composites with different volume fractions with and without additive materials at 1 MHz–1 GHz frequencies are presented and discussed.

## 2. EXPERIMENTAL

Fabrication of the 0-3 type composite materials was carried out with ceramic filler loading of approximately 20 vol.% where different additives of 2, 4 and 6 vol.%, shown in Table 1, were applied. Additionally, reference composites without additives were fabricated with 18.7–28.0 vol.% of ceramic. Thermoplastic ER140

**Table 1.** Properties of nanoparticles.

Material	Powder density	Average particle size
Silver — nAg	2.70 g/cm <sup>3</sup>	41 nm
Silicon — nSi	2.33 g/cm <sup>3</sup>	60 nm
Al <sub>2</sub> O <sub>3</sub> — nAl <sub>2</sub> O <sub>3</sub>	3.90 g/cm <sup>3</sup>	100 nm
		(rule length)

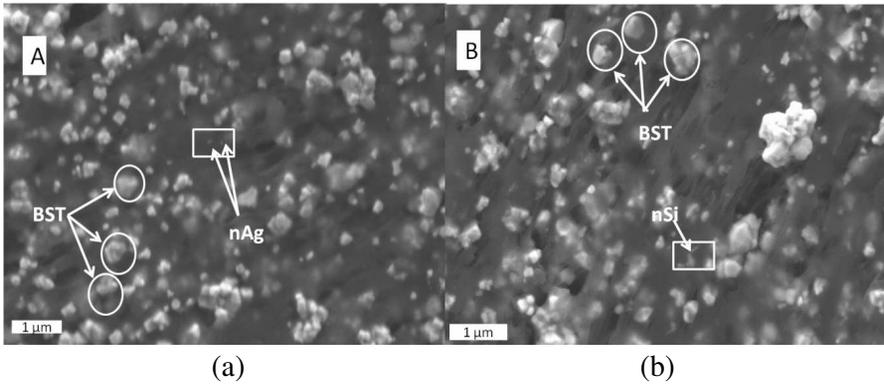
(polypropylene-graft-poly (styrene-stat-divenylbenzene), was used as a polymer matrix (NOF Co., Japan,  $\rho = 0.93 \text{ g/cm}^3$ ,  $T_{melt} = 170 \text{ }^\circ\text{C}$ ,  $\varepsilon_r = 2.2$ ,  $\tan \delta = 0.0005$  at 2 GHz) and as a high permittivity filler material Ba<sub>0.55</sub>Sr<sub>0.45</sub>Ti<sub>1.01</sub>O<sub>3</sub> (BST, Praxair Specialty Ceramics, USA,  $\rho = 5.34 \text{ g/cm}^3$ ,  $D_{50} = 1.23 \text{ } \mu\text{m}$ ,  $\varepsilon_r = 2112$ ,  $\tan \delta = 0.002$  at 100 kHz) in the paraelectric state was used.

The nanosized powders were dry mixed with BST powder after which the compounding was done with Haake Minilab twin-screw mixing extruder (Thermo, Electron Corporation, Germany) at 220 °C temperature for 30 min to achieve homogeneous dispersion throughout the composite material. Samples for the dielectric measurements were injection molded with Haake Minijet (Thermo, Electron Corporation, Germany) into circular plates with 18 mm diameter and thickness of 1 mm. In the injection molding the temperature of the heating cylinder and mould were 220 °C and 80 °C while injection and post pressures were 65 MPa and 70 MPa, respectively. The electrodes, ~ 250 nm thick Ag film, for the samples were deposited with a PVD system (Torr International Inc., USA). The final filler volume fractions of the composites, assuming that the amount of additive material does not change during fabrication process, were analyzed with a pycnometer (Gay-Lussac BlauBrand<sup>®</sup>, Brand GmbH + Co KG, Germany) by the Archimedes method [16].

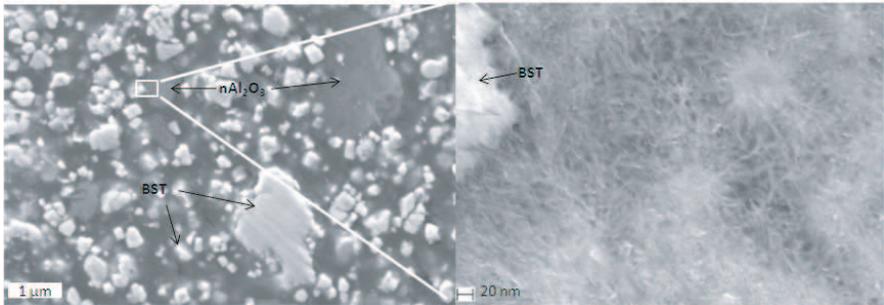
The microstructures of the composites were characterized by FESEM, (Zeiss ultra Plus FESEM, Carl Zeiss SMT AG, Germany) to investigate the particle distribution and composite morphology. The relative permittivity and dielectric losses were measured between 1 MHz and 1 GHz using an Agilent E4991A RF Impedance/Material analyzer (Agilent Technologies Inc., USA) with a 16453A dielectric material test fixture.

### 3. RESULTS

Close to homogeneous distribution (Figure 1) of the BST (white particles) particles in the polymer matrix (dark background) were



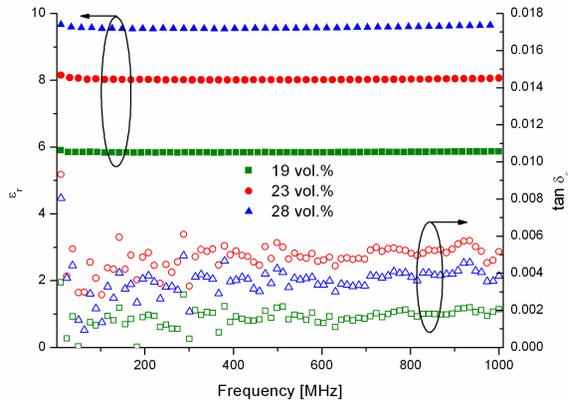
**Figure 1.** Microstructures of BST-ER140 composites with (a) 4 vol.% of nAg and (b) nSi addition.



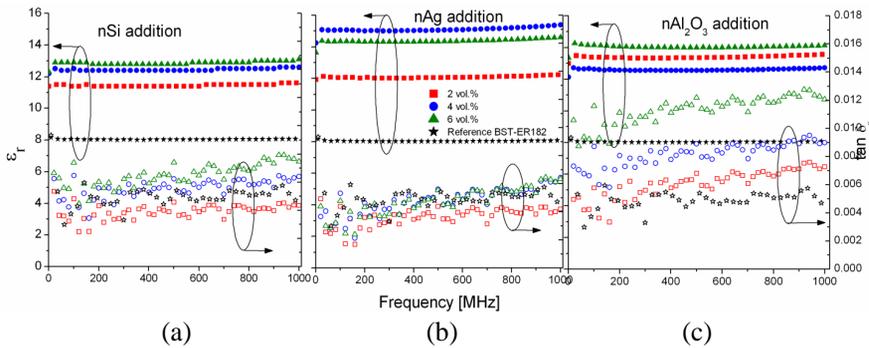
**Figure 2.** Microstructures of BST-ER140 composites with 4 vol.% of nAl<sub>2</sub>O<sub>3</sub> addition (square area enlarged).

observed, although in all composites some ceramic agglomerates could be located.

These agglomerates were less than 2 μm in diameter thus they can be and were considered mainly as primary ceramic particles since the average particle size of the ceramic was ~ 1.23 μm. Closer investigation of the samples revealed homogenous distribution of nSi and nAg additions (squared) in the BST-ER140 composite (Figures 1(a) and 1(b)). In the composite with 4 vol.% of nAl<sub>2</sub>O<sub>3</sub> addition (Figure 2) the nanofibres were clustered into larger stacks with diameter of 0.5–2 μm. These clusters caused some porosity of the samples, especially when inclusion of the nAl<sub>2</sub>O<sub>3</sub> fibres were more than 2 vol.%, due to the air trapped between the fibres, thus decreasing effective the permittivity and dielectric losses.



**Figure 3.** Dielectric properties of the BST-ER140 composites without nanoparticles additions.



**Figure 4.** Dielectric properties of BST-ER140 with different addition volumes of (a) nSi, (b) nAg, (c) nAl<sub>2</sub>O<sub>3</sub> and reference composite with 23 vol.% of BST as a function of frequency.

Figures 3 and 4 show the measurement results of the reference composites with varying ceramic volume fractions and composites with different nanosize inclusions and volumes. The reference samples without nanoparticle additions exhibited very low frequency dispersion of relative permittivity and dielectric losses.

The frequency behavior of the composites with nanosize additions had good correspondence with the reference composite, regardless of the type and volume fraction of the inclusions. However, even small amounts of nanosized materials produced higher relative permittivity with only a slight increase in the dielectric losses in all cases. For example, samples with 2 vol.% of nSi and nAg additions exhibited

**Table 2.** Measured filler loadings and dielectric properties at 1 GHz.

Composite	Additive	Add	Meas. BST	Total filler	$\epsilon_r$	$\tan \delta$
		loading [vol.%]	loading [vol.%]	loading [vol.%]		
BST-ER140 + Add	nSi	2	17.6	19.6	11.59	0.0044
		4	15.0	19.0	12.61	0.0063
		6	16.4	22.4	13.06	0.0074
	nAg	2	21.5	23.5	12.24	0.0042
		4	22.6	26.6	15.38	0.0063
		6	20.8	26.8	14.60	0.0063
	nAl <sub>2</sub> O <sub>3</sub>	2	22.2	24.2	13.56	0.0072
		4	18.7	22.7	12.71	0.0090
		6	16.9	22.9	14.13	0.122
BST-ER140	-	-	18.7	18.7	5.87	0.0018
	-	-	22.9	22.9	8.06	0.0047
	-	-	28.0	28.0	9.65	0.0037

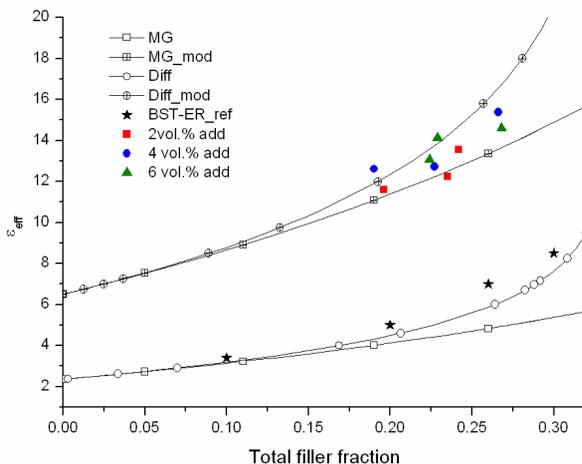
dielectric losses at the same level compared to the reference sample with 22.9 vol.% of BST (Table 2) while the relative permittivity was increased by 44–52%.

#### 4. DISCUSSION

The effective permittivity of two phases composite can be approximated with classical dielectric mixing rules, Maxwell-Garnett (MG) and Bruggeman [17, 18], or with the new differential (Diff) mixing equation presented by Jylhä et al. [19]. In Figure 5 calculations with Maxwell-Garnett and differential equations for reference samples shows quite good agreement with the measured relative permittivity.

In order to adjust the Maxwell-Garnett and differential approximations into the composites with nanoparticles the initial permittivity of matrix had to be increased from 2.35 to 6.50 in the calculations, after which the approximations fit nicely with the measured values.

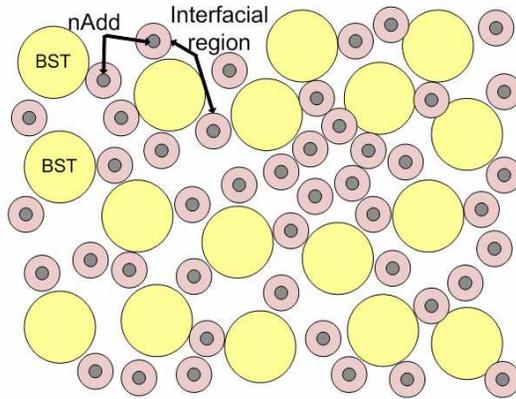
Typically in the polymer composites addition of conductive particles will increase conductivity through the polymer matrix thus modifying the distribution of electric field in the BST particles and increasing the effective permittivity [20]. However, continuous networks of nanoparticles could not be observed in the microstructures (Figures 1–2) which would also be seen as a rapid increase in the dielectric losses. In addition, the calculated average particle-particle



**Figure 5.** Effective permittivity at 1GHz of the reference BST-ER140 composites and composites with 2–6 vol.% nanoparticle/-fiber additions and calculated effective permittivity according to Maxwell-Garnet (MG) and differential effective medium theory (Diff) mixing rules as a function of total filler fraction.

distance [21] for BST was  $\sim 700$  nm (Figure 2) which is far from tunneling distances, for example 1.8 nm in CNT-epoxy composites [22]. On the other hand inclusions with higher conductivity than that of the matrix will also result interfacial or Maxwell-Wagner-Sillars polarization which has a major influence in the acoustic frequency regime, i.e., 10 Hz–1 MHz. Thus it is not expected to have a major contribution in the results especially due to stable characteristics as a function of frequency [11, 12]. Therefore the effect is expected to be result of addition of nanosize particles with large specific surface area. This leads to an exceptionally large interfacial area (Figure 6), where the electrical properties are somewhere between the bulk properties of filler and matrix. Thus large area of the polymer matrix has altered properties [23, 24].

In such case nanoparticles will introduce twofold enhancement, as a particle with higher permittivity than the matrix and as a modifier of the polymer matrix which has a dominating influence on the effective permittivity via improved coupling of the matrix and primary particles. Furthermore, even at the low volume fractions of the nanoparticles (2–6 vol.%) the entire matrix can actually be interfacial region [25]. Nevertheless, further investigations on the origin of the enhancement are still required.



**Figure 6.** Schematic of the composite microstructure.

## 5. CONCLUSION

In summary, 0-3 type BST-ER140 thermoplastic ceramic-polymer composites with three different additive materials (nSi, nAg, nAl<sub>2</sub>O<sub>3</sub>) and volume fractions were fabricated with mixing extrusion and injection molding techniques. Dielectric properties of the composites at 1 MHz–1 GHz were investigated showing significant increase of relative permittivity with all additives while the dielectric losses and frequency dispersion were at similar level with the sample without additives. Especially nanosilver addition was observed to be effective to increase the permittivity of the composites, where only 2 vol.% addition was able to enhance ( $\epsilon_r = 12.24$ ,  $\tan \delta_e = 0.0042$ ) by 52% without increasing the dielectric losses when compared to the reference ( $\epsilon_r = 8.06$ ,  $\tan \delta_e = 0.0047$ ) sample. The increase in permittivity is expected to be due to increased interphase area between matrix and nanosize filler. Furthermore, the results suggest significant reduction of filler loading by utilization of Si and Ag nanoparticles thus improved mechanical properties can be expected. If the nanofibers are used to enhance the dielectric properties, use of dispersant should be researched, in order to prevent the fibre agglomeration.

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