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Fabrication and properties of composites from BST and polypropylene-*graft*-poly(styrene-*stat*-divinylbenzene)

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Abstract

In this work, ceramic–polymer composites were fabricated from barium strontium titanate powder (BST) and polypropylene-*graft*-poly(styrene-*stat*-divinylbenzene) (ER) using a twin-screw extruder. The compounding process was characterized by rheological measurements. The effects of volume loading of BST on dielectric and mechanical properties were investigated. The dielectric properties were measured as a function of frequency and BST loading. For example, the relative permittivity and loss tangent ($\tan\delta$) of the BST–ER composites at 1 GHz were gradually increased from 2.4 and 0.0001 to 28.5 and 0.0085, respectively, as the loading was increased from 0 to 50.5 vol.%. Stearic acid (StA) was used as a surface-modifier of the BST. With an approximate surface coverage of 83%, an improvement in processability and a slight increase of the permittivity was observed, while $\tan\delta$ remained low. The excellent dielectric characteristics of these composites, with high permittivity and low $\tan\delta$, make them attractive novel electronic materials for high frequency applications.

Keywords: Extrusion; Ceramic–polymer composites; Dielectric properties; Mechanical properties; Functional applications

1. Introduction

Materials employed in microwave devices and packages need to satisfy various requirements, such as low dielectric loss, appropriate relative permittivity, low moisture absorption, as well as suitable mechanical stiffness and a low coefficient of thermal expansion. Recently, there has been huge interest in 0–3 ceramic–polymer composites because they are able to fulfill these demands. Composites using polymers such as PVDF (polyvinylidene fluoride), P(VDF-TrFE), silicone rubber, polyimides, polyvinylchloride, cyanoethylated cellulose, polystyrene, and polyurethane have been investigated.[1–8] One additional advantage available especially with thermoplastic–ceramic composites is a simple, 3D fabrication process such as injection moulding of electronic components. The authors have reported the dielectric properties of the barium strontium titanate (BST) and thermoplastic polyphenylene sulphide (PPS) and cycloolefine copolymer (COC) composites that possess low dielectric loss at high frequencies.[9,10]

In this work, 0–3 ceramic–polymer composites were fabricated from barium strontium titanate (BST) and polypropylene-*graft*-poly(styrene-*stat*-divinylbenzene) (ER). ER is a novel polymer alloy with excellent dielectric properties (low relative permittivity and low loss in the GHz region) based on polypropylene and polystyrene, which shows relatively high thermal stability and processability.[11] The effects of volume loading of BST powder on the dielectric and mechanical properties were investigated. Another task is to research the effect of coating the particle surface with stearic acid on the rheological, dielectric and mechanical properties of the composites.

2. Experimental procedures

Barium strontium titanate (BST) with a composition of $Ba_{0.55}Sr_{0.45}TiO_3$ and polypropylene-*graft*-poly(styrene-*stat*-divinylbenzene) (Dammondex® ER140, denoted as ER) were supplied from Praxair Inc. (USA) and NOF Co. (Japan), respectively. Stearic acid (StA) (Sigma–Aldrich Chemie GmbH, Germany) and ethanol (A Grade; Altia Oyj, Finland) were used for the coating of the particles.

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Composites of BST and ER were fabricated using a small-scale twin-screw extruder (HAAKE MiniLab Rheomex CTW5, Thermo Scientific, Inc., USA). In compounding, the barrel temperature was set at 220 °C. ER was first supplied to the compounding machine and melted for 10 min at a rotation rate of 60 rpm under circulation. BST powder was then added in portions. After the addition of the BST powder was completed, the mixture was kneaded for a further 30 min to render it as homogeneous as possible. Finally, the composite melt was extruded out from the die. Also the composite melt remaining in the circulation bypass was collected. Both the extrudate and the collected composite from the bypass were cut into granules. Ceramic loadings of the composite samples were measured by pycnometry.

The surface modification of BST by StA was done starting with 30 g of BST powder placed in a beaker with the addition of 30 ml ethanol. The mixture was mixed well using a spatula to remove air bubbles. Then the calculated amount (0.24 g, 5 vol.% to BST volume) of StA was added to the mixture and stirred for 5 min, after which the beaker was covered by a watch glass and placed in a convection oven set at 70 °C. After 60 min, the mixture was mixed well again to ensure uniformity of treatment. Finally, the mixture was dried in the oven to produce the surface-modified BST powder.

Samples for dielectric and mechanical measurements were fabricated by an injection moulding machine (HAAKE MiniJet, Thermo Scientific, Inc., USA). The temperature of the cylinder and the mould were maintained at 220 and 70 °C, respectively. Plunging pressure was set at 700 Pa. Rounded-square-shaped samples with 18 mm side-length and 1.2 mm thickness were prepared for the dielectric measurement. Dumbbell-shaped samples were prepared for the mechanical testing.

Rheological properties were measured from the torque of the screws at various rotation rates and pressure loss in the circulation bypass at 220 °C with the aid of a PC application (HAAKE Polylab Minilab Software, Thermo Scientific, Inc., USA). Relative permittivity (ε') and dielectric loss ($\tan\delta$; $\varepsilon''/\varepsilon'$) were measured using an RF impedance/material analyzer (E4991A equipped with 16453A fixture, Agilent Technologies, Inc., USA) at a frequency range of 10 MHz to 1 GHz. Tensile properties were measured by a universal testing machine (Instron Universal Testing Machine Model 5544, Instron Co., USA). Microstructures of the composites were studied by scanning electron microscopy (SEM, JSM-6400, JEOL Ltd., Japan).

3. Results and discussions

Generally higher loadings of dielectric filler are required when a higher relative permittivity is needed. However, higher loading increases viscosity and thus surface modification of fillers by surfactants or coupling agents is commonly used to improve particle dispersion in a polymer matrix and also the rheological properties of a compound consisting of such matrices. Surface modification of the filler can, on the other hand, have an effect on dielectric and mechanical properties of the compound and thus the optimum amount needs to be researched to produce composites fulfilling product established requirements. In this work, StA was selected as the surface-modifier because of its special molecular structure with one end R-COOH possibly attaching to a Ba or Ti ion of the filler.[12] StA is also used in industrial filler–polymer composites to improve processability.[13]

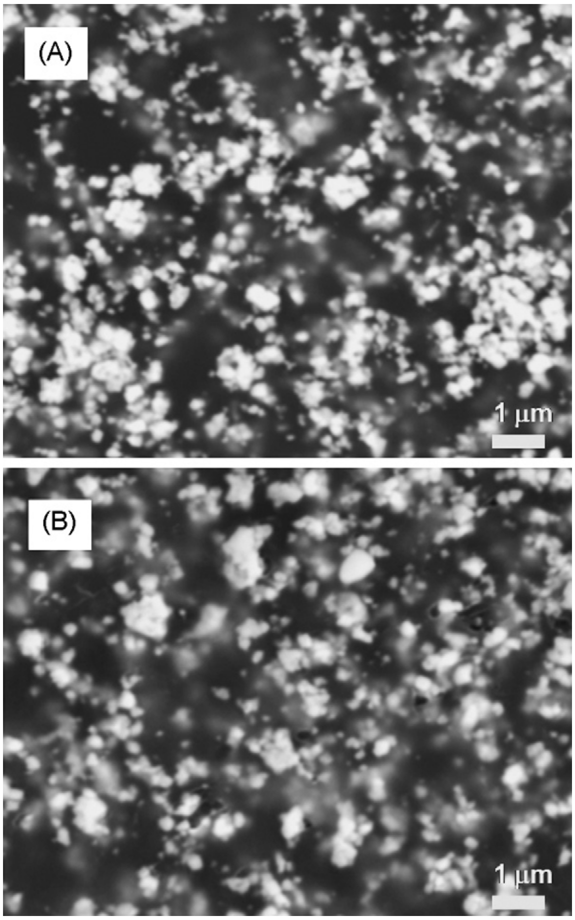

Fig. 1. SEM pictures of the surface of a composite from untreated BST (A) and StA-treated BST (B).

Four different composites with different loadings were prepared for both untreated and StA-treated BST powders. The composites were numbered as N1 to N4 and T1 to T4, respectively, with BST loadings set from about 20 up to 50 vol.% in feed. StA addition was kept at 5 vol.% to BST.

3.1. Microstructure of the composites

SEM images of the polished surfaces of composites from untreated BST powder (N1) and StA-treated BST powder (T1) are shown in Fig. 1(A) and (B), respectively. There are found to be some agglomerates of filler particles in the untreated BST composite (A). On the other hand, fewer agglomerates were found in the StA-treated BST composite. From these photographs it can be concluded that surface modification by StA considerably improves the filler dispersion condition in the composites.

3.2. Rheological properties of the composites

Rheological properties of N1, N3, T1, and T3 with loading levels of 22.0, 36.8, 17.7, and 37.2 vol.%, respectively are shown

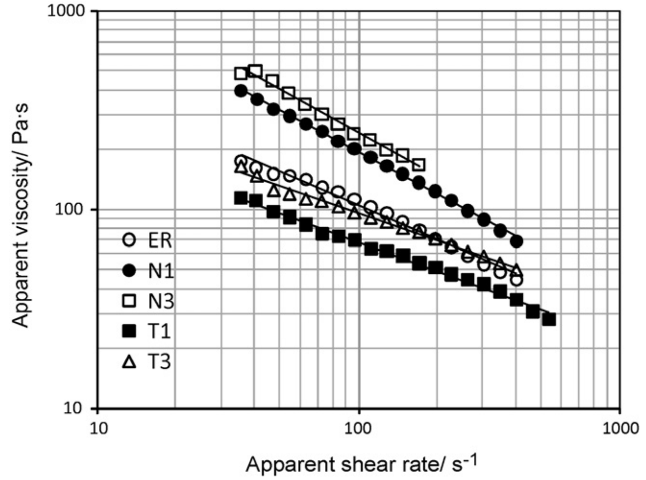

Fig. 2. Apparent viscosity dependence on apparent shear rate of ER and the composites from both untreated (N1 and N3) and StA-treated (T1 and T3) BST powders (logarithmic plot).

in Fig. 2. In all cases, the logarithms of apparent shear rate (γ) and apparent viscosity (η) are in a nearly linear relationship, therefore it is suggested that ER and its composites present typical pseudoplastic flow in the γ range of 35–400 s^{-1}. As shown in Fig. 2, η gradually increases as the untreated BST loading increases (N1 to N3). However, the StA coating decreased the apparent viscosity effectively and thus processing of both composites with treated BST powders (T1 and T3) are easier than processing the pure polymer. When the loading level of treated BST powder is moderate (T1), the γ of the composite is clearly reduced, but it starts to increase with increased loading (T3). Actually the viscosity of T3 is almost equal to that of ER. The reason for this is believed to be caused simply by increased loading, as in the case of untreated fillers (compare N1 and N3). However, with these treated ceramic fillers the intrinsic viscosity level (T1) is low. Further addition of StA is not expected to improve the situation because according to the specific surface area of BST (4.18 m^2/g) and the molecular occupation of a StA molecule (0.205 nm^2),[14] the theoretical surface coverage is calculated to be ~83%.

3.3. Dielectric properties of the composites

The average values of relative permittivity and loss tangent measurements at 0.97–1 GHz are summarized in Fig. 3. When surface-treated BST was used (T1–4), a slight increase in the relative permittivity was observed, while there was no significant effect on the tan δ.

The relative permittivities of the BST–ER composites with and without StA treatment were applied to the modified Lichtenecker's logarithmic equation[15]:

$$\log\varepsilon = \log\varepsilon_p + v_b(1-k)\log\left(\frac{\varepsilon_b}{\varepsilon_p}\right). \tag{1}$$

where k is an empirical fitting constant of the composites, v_b is the volume fraction of the ceramic, and ε_p and ε_b are the relative permittivities of the matrix polymer and ceramic, respectively. In this study, ε_p and ε_b were 2.37 and 2543, respectively at 1 GHz. The experimental data are fitted to the equation by the least-squares method. As a result of the fitting, k values of 0.27 and 0.29, with coefficients of correlation R^2 of 0.9992 and 0.9978 were obtained for the BST–ER composites with and without surface modification, respectively.

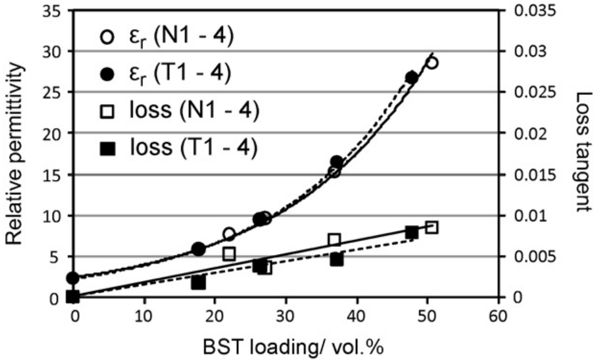

Fig. 3. Relative permittivity and loss tangent of the composites with untreated (○, □) and StA-treated (●, ■) BST powders at 0.97–1 GHz.

From our earlier result employing PPS and COC as the matrix polymer,[9,10] k of 0.37 and 0.43 were obtained, respectively. It is also reported that $k = 0.3$ for well-dispersed ceramic–polymer composites.[15] On the other hand, it was suggested that de-agglomeration of dielectric filler particles leads to a higher permittivity of composites.[16] Considering those previous reports, the results obtained in this study would indicate that ER polymer improves filler dispersion in comparison to PPS and COC. The slight decrease of parameter k from 0.29 for the composites without modification to 0.27 for the composites with StA-modification would indicate also that the surface modification by StA accelerates the filler dispersion during the compounding process and improves the particle dispersion in the resulting composites.

3.4. Mechanical properties of the composites

The results of the tensile tests are summarized in Fig. 4. It is shown that increasing the loading of BST makes the Young's

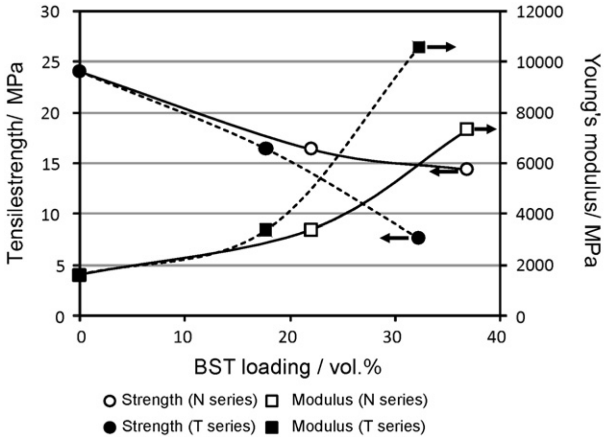

Fig. 4. Tensile strength (○ for untreated and ● for StA-treated) and Young's modulus (□ for untreated and ■ for StA-treated) of the composites.

modulus gradually increase. Also it was observed that the tensile strength was decreased as the loading increased. It is well-known that spherical fillers generally enhance the modulus of a composite while they cause a remarkable decrease both in elongation prior to breaking and in tensile strength.[17,18] From comparison of the properties of untreated and StA-treated BST composites, it was observed that the elastic modulus of the T series (StA modified) samples increases more rapidly with increasing loading than that of the N series (untreated). Furthermore, the tensile strength of the composites of the T series is lower than that of the N series. The former result can be explained by the existence of a boundary layer around a particle embedded in a polymer matrix. Molecular conformation in the boundary layer is limited to give a higher modulus than in an unaffected matrix and the thickness of this boundary layer is influenced by compatibility between the surface and the matrix.[19] In the case of the composites from StA modified powder, particles are well dispersed therefore the area of the boundary can be larger than that of untreated BST composites. Moreover, the layer can be thicker due to its higher compatibility with the matrix. Thus it can be supposed to have a higher content of the boundary layer with higher modulus. Therefore the tensile modulus can be increased when the surface is modified by StA.

The latter result is rather contradictory to that of previous research.[20] Since StA has no functional group that reacts with the matrix, the adhesion strength between the surface and the surrounding polymer is supposed to be poor. This is the same with an untreated BST surface. Consequently, there should be no difference in tensile strength between the two cases. The observed difference in tensile strength might come from uncertain experimental error such as micro-crack formation. More experiments should be done to explain this phenomenon.

4. Conclusion

In this work, we have fabricated 0–3 ceramic–polymer composites from BST and ER, and their rheological dielectric and mechanical properties are characterized. We have also investigated the effect of surface-coating by StA on the aforementioned properties of the composites. As a result, we confirmed that surface modification by StA greatly reduces the apparent viscosity of a BST–ER composite. We also confirmed that BST–ER composites show good dielectric properties with low loss, and their relative permittivities accord to the modified Lichtenecker's logarithmic equation with a k factor of 0.29. It was found that surface-coating with StA slightly increases the relative permittivity of the composites without increasing their dielectric loss.

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