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$MgTiO_3$/polystyrene composites with low dielectric loss

Dong Hyeok Im, Chang Jun Jeon, Eung Soo Kim *

Department of Materials Engineering, Kyonggi University, Suwon 443-760, Republic of Korea

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Abstract

Composites of $MgTiO_3$ filler dispersed inside polystyrene (PS) matrix were prepared by extrusion method and hot-molding technique. Effects of particle size of $MgTiO_3$ on the dielectric properties of $MgTiO_3$/PS composites were investigated at microwave frequencies. With increasing of $MgTiO_3$ content, the apparent density of the composites was increased, while the relative density was decreased due to the increase of porosity, which induced the increase of dielectric loss (tan δ) of the composites. The tan δ of the composites was also affected by the mixture ratio of $MgTiO_3$ with different particle sizes. The dielectric constant (K) and temperature coefficient of resonant frequency (TCF) of the composites with $MgTiO_3$ content and particle size were also discussed.

Keywords: A. Hot pressing; B. Composites; C. Dielectric properties; $MgTiO_3$/polystyrene

1. Introduction

Recently, there has been an upsurge in demand for ceramics/polymer composites with high-performance which have low dielectric constant (K) and dielectric loss (tan δ) for fast signal speed and low delay time of propagation. because they are available to the various applications such as packages and substrate materials.

It has been reported that polystyrene (PS) has low-processing temperature (160 °C), good flexibility and excellent microwave dielectric properties ($K = 2.14$, $\tan\delta = 4 \times 10^{-4}$) [1], comparing with other polymer such as polyvinylidene fluoride, polymethyl methacrylate, polyacetylene, and polyanilene. In our preliminary experiment, $MgTiO_3$ ceramics sintered at 1350 °C for 3 h showed good microwave dielectric properties ($K = 18.2$, $\tan\delta = 0.3 \times 10^{-4}$) [2]. Therefore, PS filled with $MgTiO_3$ ceramics would be an effective approach to improve the dielectric properties of ceramics/polymer composites for packages and substrate applications.

Generally, the dielectric properties of ceramics/polymer composites could be controlled effectively by the amount and type of ceramics. Also, the degree of dispersion and the connectivity of the constituents in the polymeric matrix were strongly affected by the particle size of ceramics, which induced the changes of the dielectric properties. Dispersion behaviors of ceramics with different particle sizes should be studied to improve the dispersion and connectivity of ceramics in the polymeric matrix.

In this study, the dielectric properties of $MgTiO_3$/PS composites were investigated based on volume fraction, particle size and mixture ratio of $MgTiO_3$ with different particle sizes. Also, the temperature coefficient of resonant frequency (TCF) of composites was discussed for thermal stability of the composites at microwave frequencies.

2. Experimental procedures

$MgTiO_3$ ceramics powder was prepared by a conventional solid-state reaction from the powders of MgO and TiO_2 (rutile) with purities above 99%. These powders were milled using ZrO_2 balls for 24 h in ethyl alcohol. To obtain a single phase of $MgTiO_3$, the mixtures were dried and calcined at 1100 °C for 5 h, and then sintered at 1350 °C for 3 h in air. The sintered powders were grinded and sieved into the powders with the particle size of about ≤45 μm and 250–300 μm, respectively. Polystyrene (PS) with molecular weight of 280,000 (gel permeation chromatography (GPC)) was used as the polymer matrix. PS was weighed and put into the chamber of the Torque Rheometer (Rheomix 600p, ThermoHaake, Germany) at 200 °C, followed by slow addition of the $MgTiO_3$ ceramics

* Corresponding author. Tel.: +82 31 249 9764; fax: +82 31 244 6300.
E-mail address: eskim@kyonggi.ac.kr (E.S. Kim).

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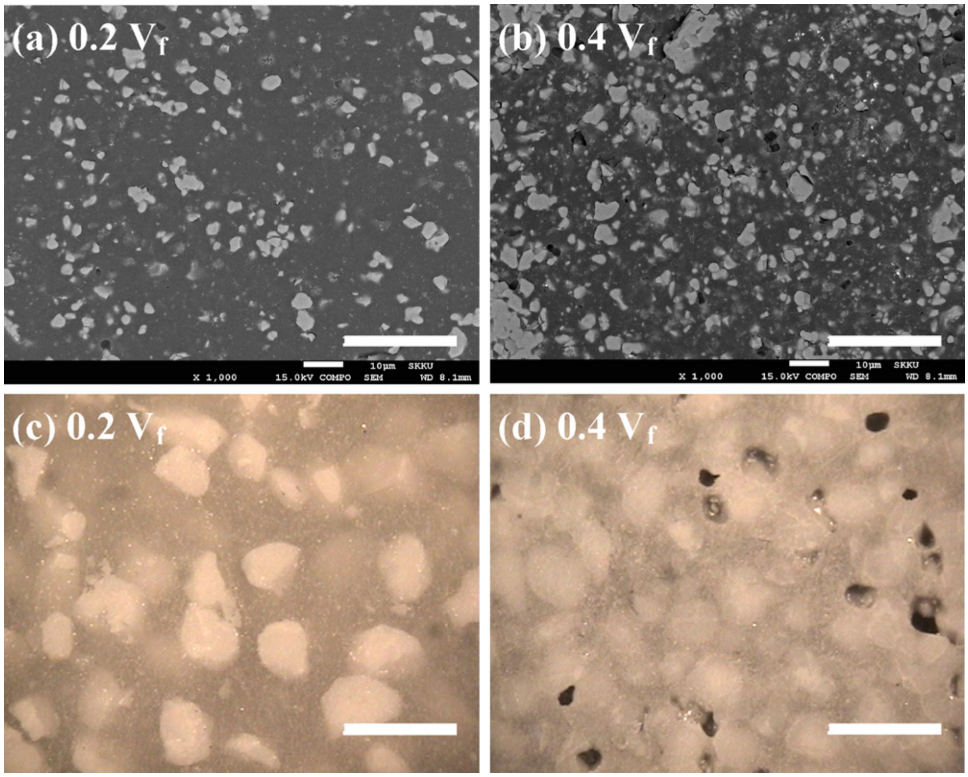

Fig. 1. SEM micrographs ((a) and (b): ≤45 μm, bar = 30 μm) and optical images ((c) and (d): 250–300 μm, bar = 700 μm) of $MgTiO_3$/polystyrene composites with volume fraction (V_f) of $MgTiO_3$.

powder. After mixing at a speed of 50 rpm for 30 min–1 h, $MgTiO_3$/PS composites were taken from the chamber and hot-pressed at 200 °C from 13 to 19 MPa for 1 h to prepare the specimens for the evaluation of physical and dielectric properties.

The apparent density of the composites was measured by Archimedes method. The relative density was obtained from the theoretical values by mixing rule. Powder X-ray diffraction analysis (XRD, D/Max-3C, RIGAKU, Japan) was used to identify the crystalline phases of the specimens. Microstructure of the specimens was observed using a scanning electron microscope (SEM, JSM-7500F, JEOL, Japan) and metallogical microscope (DCS-105, Sometech, Korea). As frequency ranges from 1 GHz to 7.3 GHz, the dielectric properties were measured by open-ended coaxial resonator probes method [3]. At 13 GHz, the dielectric properties were measured by the Hakki and Coleman method [4]. The temperature coefficient of resonant frequency (TCF) was measured by the cavity method [5] in the temperature range from 25 °C to 80 °C at 8 GHz.

3. Results and discussion

SEM micrographs and optical images of $MgTiO_3$/polystyrene (PS) composites with volume fraction (V_f) and particle size of $MgTiO_3$ are shown in Fig. 1. With increasing of $MgTiO_3$ content, the distance between $MgTiO_3$ particles was decreased and connectivity was increased. The interface areas between PS and $MgTiO_3$ with particle size of ≤45 μm (Fig. 1(a) and (b)) were larger than those with particle size of 250–300 μm (Fig. 1(c) and (d)). For the composites with low V_f of $MgTiO_3$, $MgTiO_3$ particles were completely surrounded by the melted PS which induced the low porosity. However, the pores were observed for the composites with $0.4V_f$ of $MgTiO_3$ (Fig. 1(b) and (d)). These results could explain that the composite materials became less compact and easily brought out pores with decreasing of PS content.

For the composites with $0.4V_f$ of $MgTiO_3$, the abbreviations for mixture ratio of small particle size (S, ≤45 μm) and large particle size (L, 250–300 μm) of $MgTiO_3$ in this study are summarized in Table 1.

Fig. 2 shows the apparent and relative densities of $MgTiO_3$/PS composites with V_f of $MgTiO_3$ (≤45 μm, 250–300 μm) and mixture ratio (≤45 μm (S): 250–300 μm (L)) at $0.4V_f$ of $MgTiO_3$, respectively. With increasing of $MgTiO_3$ content, the apparent density of the composites was increased due to the higher density of $MgTiO_3$ (3.895 g/cm^3) than that of PS (1.05 g/

Table 1
Mixture ratio of small particle size (S, ≤45 μm) and large particle size (L, 250–300 μm) for the composites with 0.4 volume fraction (V_f) of $MgTiO_3$.

Abbreviation	Volume fraction (V_f) of $MgTiO_3$	
	S (≤45 μm)	L (250–300 μm)
S0:L4	0	0.4
S1:L3	0.1	0.3
S2:L2	0.2	0.2
S3:L1	0.3	0.1
S4:L0	0.4	0

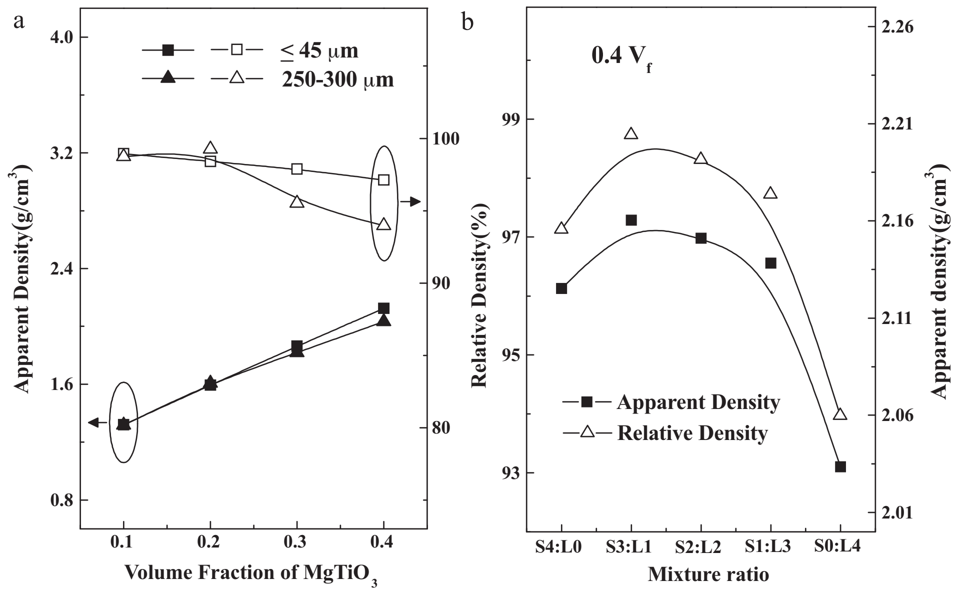

Fig. 2. Apparent and relative densities of $MgTiO_3$/polystyrene composites with (a) volume fraction (V_f) of $MgTiO_3$ (≤45 μm, 250–300 μm) and (b) mixture ratio (≤45 μm (*S*): 250–300 μm (*L*)) at $0.4V_f$ of $MgTiO_3$.

cm^3), while the relative density was decreased above $0.2V_f$ due to the increase of porosity by weak adhesion of interface between $MgTiO_3$ and PS. For the composites with $MgTiO_3$ above $0.2V_f$, the relative density of the composites with large size of $MgTiO_3$ (250–300 μm) was smaller than that of the composites with small size of $MgTiO_3$ (≤45 μm) due to the large porosity, as confirmed in Fig. 1(b) and (d). For the composites with various mixture ratio at $0.4V_f$ of $MgTiO_3$, the apparent and relative densities of the composites were increased up to S3:L1 and then decreased at S4:L0. These results could be explained that the pores between large particle size of $MgTiO_3$ were filled with small particle size of $MgTiO_3$. Also, the apparent and relative densities of the composites with homogeneous particle size of $MgTiO_3$ (S4:L0, S0:L4) were smaller than those of the composites with heterogeneous particle size of $MgTiO_3$ (S3:L1, S2:L2, and S1:L3).

Fig. 3 shows the XRD patterns of $MgTiO_3$/PS composites with volume fraction (V_f) of $MgTiO_3$ (250–300 μm) and mixture ratio at $0.4V_f$ of $MgTiO_3$, respectively. The trigonal ilmenite structure (*R-3H*) of $MgTiO_3$ and amorphous halo of PS were confirmed through the entire range of compositions. Based on the XRD patterns of the specimens, the reaction

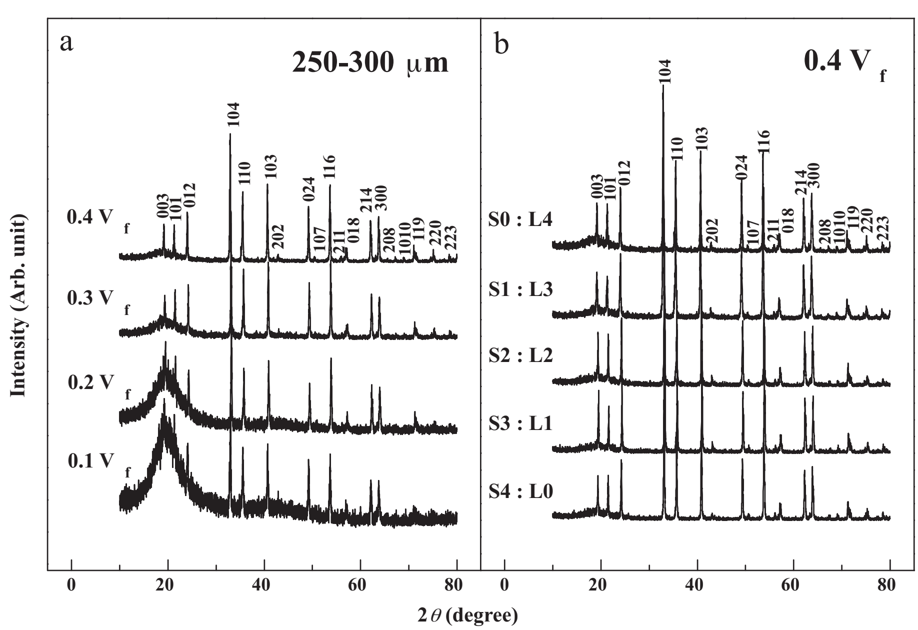

Fig. 3. X-ray diffraction patterns of $MgTiO_3$/polystyrene composites with (a) volume fraction (V_f) of $MgTiO_3$ (250–300 μm) and (b) mixture ratio (≤45 μm (*S*): 250–300 μm (*L*)) at $0.4V_f$ of $MgTiO_3$.

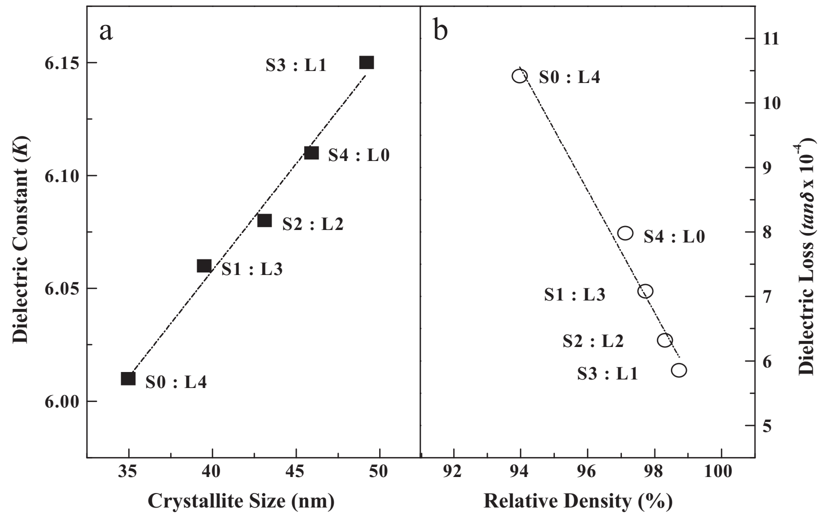

Fig. 4. Dependence of (a) dielectric constant (K) and/or (b) dielectric loss (tan δ) on the crystallite size and/or relative density with mixture ratio ($\leq$45 μm (S): 250–300 μm (L)) at $0.4V_f$ of $MgTiO_3$ (13 GHz), respectively.

compounds between $MgTiO_3$ and PS were not detected, which in turn, the chemical reactions between the $MgTiO_3$ and PS were not observed. With increasing of $MgTiO_3$ (250–300 μm) content, the amorphous halo of PS was decreased, while the intensity of crystalline $MgTiO_3$ phase was increased (Fig. 3(a)). For the composites with various mixture ratio at $0.4V_f$ of $MgTiO_3$, the intensity of crystalline $MgTiO_3$ phase and amorphous halo of PS were also changed slightly with different mixture ratios (Fig. 3(b)). These results are due to the different crystallinity of the composites. Therefore, the crystallite size of the composites was calculated from the full width at half maximum (FWHM) intensity of the XRD peak ($2\theta = 32.9°$) using Scherrer's equation [6] for the evaluation of the crystallinity of the composite.

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

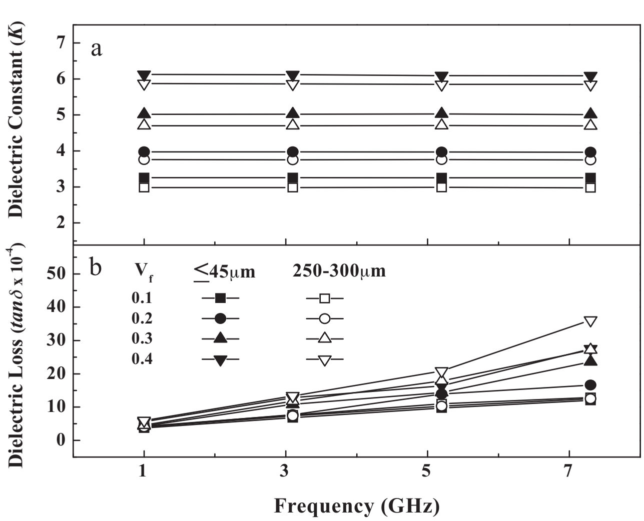

Fig. 5. Frequency dependence of (a) dielectric constant (K) and (b) dielectric loss (tan δ) of $MgTiO_3$/polystyrene composites with volume fraction (V_f) of $MgTiO_3$ ($\leq$45 μm, 250–300 μm).

where λ is the wavelength of the X-ray radiation ($\lambda = 0.154$ nm), B is the FWHM of the peak (radians) corrected for instrumental broadening, θ is the Bragg angle, and D is the crystallite size (nm).

Fig. 4 shows the dependence of dielectric constant (K) and/or dielectric loss (tan δ) on the crystallite size and/or relative density with mixture ratio at $0.4V_f$ of $MgTiO_3$ (13 GHz), respectively. With increasing of $MgTiO_3$ with small particle (S), the K of the composites was increased except for mixture ratio of S3:L1 which was dependent on the crystallite size. However, the tan δ of the composites was decreased with increasing of $MgTiO_3$ with small particle (S) except for mixture ratio of S4:L0. These results could be attributed to the decrease of relative density by the formation of pore, as confirmed in Fig. 1.

Fig. 5 shows the frequency dependence of K and tan δ of $MgTiO_3$/PS composites with V_f of $MgTiO_3$ ($\leq$45 μm, 250–300 μm). For all of the V_f and particle size, the K of the composites showed a constant with frequency from 1 GHz to 7.3 GHz. However, the K of the composites was increased with $MgTiO_3$ content at same frequency. These results are due to the increase of the dipole–dipole interaction and connectivity among $MgTiO_3$ particles with $MgTiO_3$ content. Also, the K of the composites with small particle size of $MgTiO_3$ ($\leq$45 μm) was larger than that of the composites with large particle size of $MgTiO_3$ (250–300 μm) due to the interfacial polarization [7]. The tan δ of the composites was increased with frequency due to the dipolar relaxation process associated with the matrices. With increasing of $MgTiO_3$ content, the tan δ of the composites was increased at same frequency. The tan δ of the composites with small particle size of $MgTiO_3$ ($\leq$45 μm) was smaller than that of the composites with large particle size of $MgTiO_3$ (250–300 μm). These results could be attributed to the interfacial polarization and density [7].

Fig. 6 shows the temperature coefficient of resonant frequency (TCF) of $MgTiO_3$/PS composites with V_f and mixture ratio of $MgTiO_3$ at 8 GHz. The TCF of $MgTiO_3$/PS composites was decreased with $MgTiO_3$ content due to the

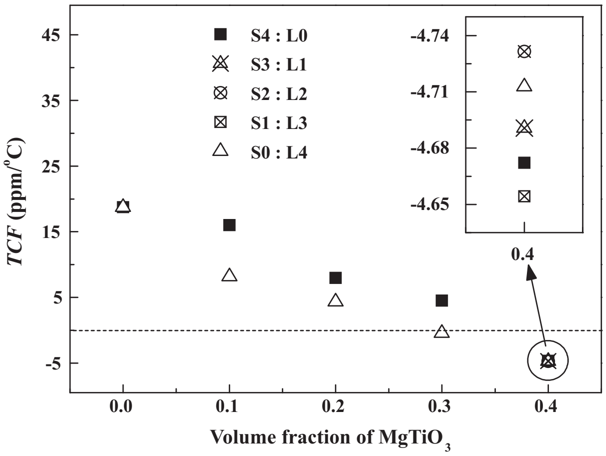

Fig. 6. *TCF* of $MgTiO_3$/polystyrene composites with volume fraction and mixture ratio (≤45 μm (*S*): 250–300 μm (*L*)) of $MgTiO_3$ at 8 GHz.

lower *TCF* of $MgTiO_3$ (−54.5 ppm/°C) than that of PS (18.74 ppm/°C). For the composites with $MgTiO_3$ from $0.1V_f$ to $0.3V_f$, the *TCF* of the composites with small particle size of $MgTiO_3$ (≤45 μm) was larger than that of the composite with large particle size of $MgTiO_3$ (250–300 μm). However, the *TCF* value of the composites was not changed with mixture ratio of $MgTiO_3$ with different particle sizes at $0.4V_f$ under investigation. Good thermal stability (zero *TCF*) was obtained for the composites with $0.3V_f$ of $MgTiO_3$ (250–300 μm).

4. Conclusions

Effects of $MgTiO_3$ on the dielectric properties of $MgTiO_3$/polystyrene (PS) composites were investigated with respect to volume fraction, particle size and mixture ratio of $MgTiO_3$ with different particle sizes. The dielectric constant (*K*) of the composites with small particle size of $MgTiO_3$ (≤45 μm) was larger than that of the composites with large particle size of $MgTiO_3$ (250–300 μm), while the dielectric loss (tan δ) of the composites with small particle size of $MgTiO_3$ (≤45 μm) was smaller than that of the composites with large particle size of $MgTiO_3$ (250–300 μm). At the frequency range from 1 GHz to 7.3 GHz, the *K* of the composites showed the good frequency stability, while the tan δ was increased with frequency. $MgTiO_3$/PS composites with mixture ratio (≤45 μm (*S*): 250–300 μm (*L*)) of S3:L1 showed maximum *K* and minimum tan δ at 0.4 volume fraction (V_f) of $MgTiO_3$. Good thermal stability (zero *TCF*) was obtained for the composites with $0.3V_f$ of $MgTiO_3$ (250–300 μm).

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