

TAILORING MICROWAVE DIELECTRIC PROPERTIES OF CERAMICS/PTFE COMPOSITE WITH MULTI-LAYERED STRUCTURES

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Abstract

Effects of connectivity patterns and multi-layered structures on the dielectric properties of polytetrafluoroethylene (PTFE) composites with low-loss ceramics ($ZnMoO_4$, $MgMoO_4$ and $MgTa_2O_6$) were investigated at microwave frequencies. Dielectric constants (K), dielectric losses ($\tan\delta$), and temperature coefficients of resonant frequency (TCF) of the composites with 0-3 connectivity patterns were dependent on the type and amount of ceramics. Multi-layered 2-2 type composites with 0.2 ceramic volume fractions (V_f) showed strong dependence of $\tan\delta$ on multi-layered structures. This was due to strain differences between different layers in the multi-layered 2-2 type composites. Several theoretical models were employed to predict the effective K of the composites and were compared with experimental data. Microwave dielectric properties can be tailored by the connectivity patterns and multi-layered structures of the composite applicable to high-performance substrate and electronic packages

1. Introduction

Ceramic / Polymer composites consisting of ceramic particles filled in a polymer matrix have been widely studied for microwave substrate and electronic packaging applications, because their mechanical flexibility, chemical stability, ease of processing and tuneable properties that allows tailoring of dielectric properties. These composites should have low dielectric constant (K) to reduce the signal propagation delay and low dielectric loss ($\tan\delta$) for better device performance at high frequency applications and microwave devices.

Up until now, most of researches have focused to search the new ceramic / polymer composite by the control of ceramic filler volume fraction and interfaces between ceramic and polymer matrix. However, the microwave dielectric properties of composites depend not only on the type and amount of the filler and the matrix but also on their connectivity pattern and multi-layered structure. The common connectivity of ceramic / polymer composites is 0–3, where the first digit refers to the dimensionality of the ceramic filler, and the second digit refers to that of the polymer matrix. Also, various approaches based on bulk processing, layer processing and melt processing have been tested in preparing functionally gradient materials and could easily be applied to the preparation of ceramic / polymer composites [1,2]. The materials with layered structure show considerable stresses if the layers have different elastic or thermal properties [3]. Thus, the strains of layers, the type of multi-layered structure and

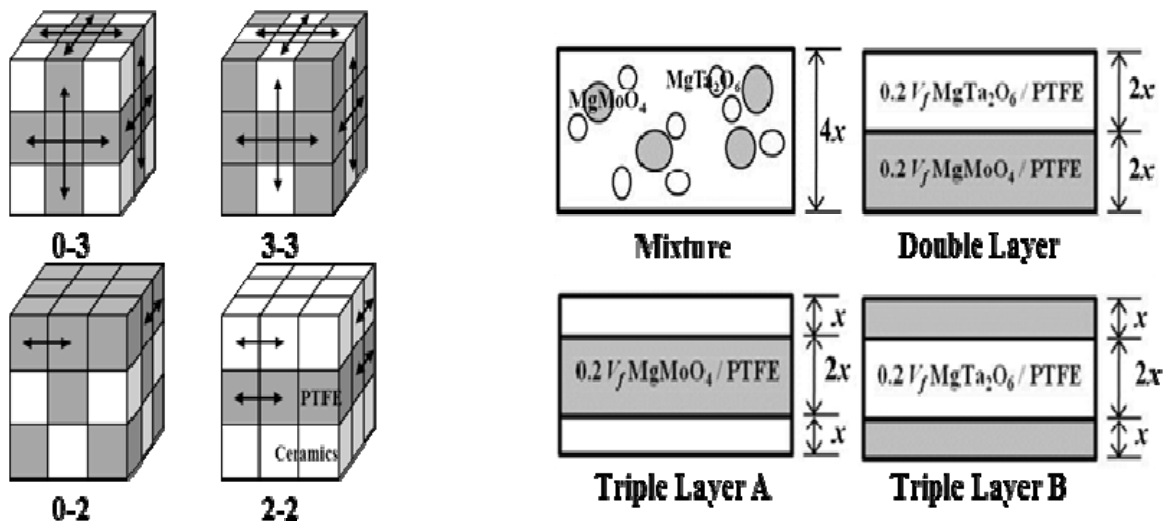
the homogeneous dispersion of the ceramic filler can affect a dielectric loss ($\tan\delta$) of the composite. Therefore, the connectivity pattern and layered structure of the composites should be considered for the electromechanical performance and for the best possible design structure of composites.

Our preliminary results showed that ZnMoO_4 , MgMoO_4 and MgTa_2O_6 had low $\tan\delta$ values above 10 GHz (ZnMoO_4 , 2.94×10^{-5} ; MgMoO_4 , 3.03×10^{-4} ; MgTa_2O_6 , 6.02×10^{-5}). Polytetrafluoroethylene (PTFE) was selected as the polymer matrix in this study because of its excellent dielectric properties ($K = 2.1$, stable up to 20 GHz; $\tan \delta = 10^{-4}$ at 800 MHz), high thermal stability (applicable up to 250°C), low moisture absorption, and good corrosion resistance [2].

Therefore, the dependence of the microwave dielectric properties on the connectivity patterns and layered structures of PTFE composites filled with ZnMoO_4 , MgMoO_4 and MgTa_2O_6 was investigated as a function of volume fraction (V_f) of ceramics. The experimental K of the composites was compared with the effective K calculated by several theoretical models.

2. Experimental Procedure

Oxide powders with high-purity above 99.9% were used as starting materials. The powders were weighed according to the compositions of ZnMoO_4 , MgMoO_4 and MgTa_2O_6 , and then milled with ZrO_2 balls for 24 h in ethanol. To obtain the single phase of each ceramic composition and the optimal microwave dielectric properties of the composites, ZnMoO_4 were calcined at 650°C for 3 h, and re-calcined again at 800°C for 3 h, while MgMoO_4 and MgTa_2O_6 were double calcined at 1350°C and 850°C for 3 h, respectively. These calcined powders were re-milled with ZrO_2 balls for 24h in ethanol and then dried. Due to the high melt viscosity ($> 10^{11}$ Pa s) of PTFE [4], the PTFE composites filled with ceramics were prepared by powder processing. The mixed composite powders were pressed isostatically into 15-mm-diameter discs with different connectivity and multi-layered structures under a pressure of 20 MPa for 1 min. The connectivity patterns and multi-layered structures of the composites are shown in Fig. 1.



(a) Connectivity Patterns

(b) Multi-layered structures

Figure 1. Schematic diagrams of connectivity patterns (a) and multi-layered structures (b) of $0.2 V_f$ ceramic / PTFE composite.

Although the connectivity patterns and multi-layered structures of the composites were changed, each specimen had the same total thickness and the same net compositional ratio ($0.2 V_f$ ceramics) to eliminate the effects of thickness and ceramic content on the microwave dielectric properties. The resulting pellets were heat treated at 300°C for 1 h. Microstructures of the composites were observed by scanning electron microscopy (SEM, JSM-6500F, JEOL, Japan). The apparent density of the composites was measured by Archimedes method. The relative density was obtained from the theoretical values by mixing rule.[5] Powder X-ray diffraction (XRD, D/Max-2500V/PC, RIGAKU, Japan) was used to determine the crystalline phases of the prepared composites. The values of K and $\tan \delta$ were measured by the Hakki and Coleman method [6] and the cavity method [7] at frequencies in the range of 10–14 GHz.

3. Results and Discussion

3.1 Effect of connectivity patterns on the microwave dielectric properties of composite

From the XRD patterns of the PTFE composites filled with various V_f of ZnMoO_4 , any compounds produced by reactions between the ceramics and PTFE were not detected, suggesting that there was no chemical reaction between ZnMoO_4 and PTFE. With increasing ceramic content, the peak intensity of PTFE decreased, while that of ceramic increased. Figure 2 shows the XRD patterns of the $0.2 V_f \text{ZnMoO}_4 / \text{PTFE}$ composites with different connectivity. The peak intensity of ZnMoO_4 was changed slightly with the connectivity patterns of the composites due to the different distributions of ZnMoO_4 particles.

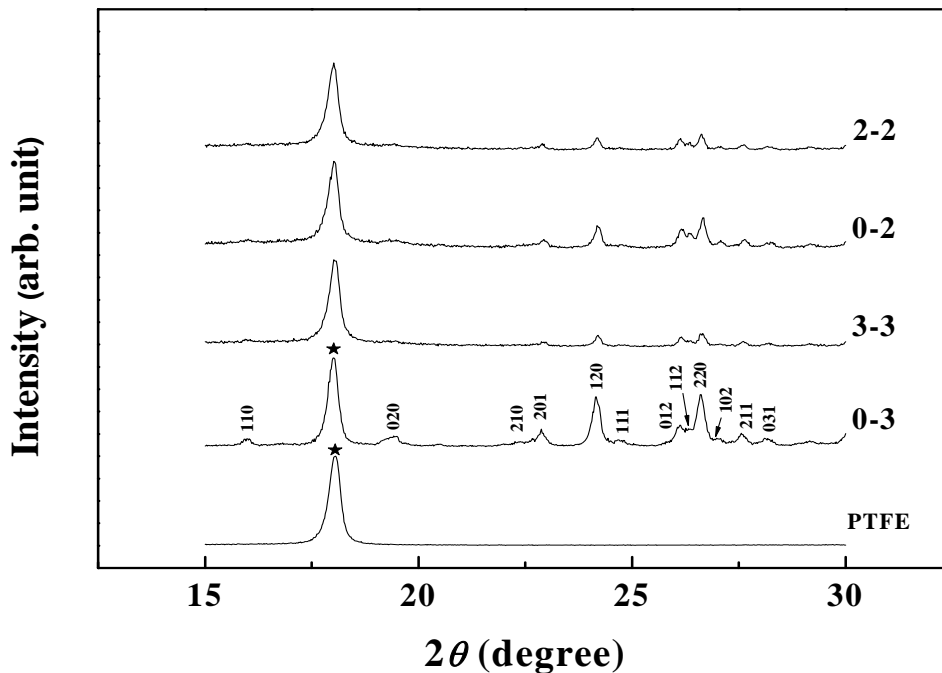


Figure 2. X-ray diffraction patterns of PTFE composites filled with $0.2 V_f \text{ZnMoO}_4$ with different connectivity.

The relative density of the 0–3 connectivity composites decreased with the ceramic content due to the increase of porosity brought about by weak adhesion at the interfaces between the ceramics and PTFE. The apparent densities of the $0.2 V_f \text{ZnMoO}_4/\text{PTFE}$ composites with different connectivity showed similar values of $2.383\text{--}2.564 \text{ g/cm}^3$. The relative densities above 91 % of the theoretical values were obtained for all of the composites with different connectivity.

The microwave dielectric properties of 0–3 connectivity composites are generally dependent on the amounts of ceramics and their dielectric properties, because ceramics show superior dielectric properties to those of polymers. However, the microwave dielectric properties of the composites with different connectivity were affected by extrinsic defects such as cracks, debonding, and diffusion between the ceramics and polymer. Although these defects were not observed by the SEM micrographs in this study, the dielectric properties of the composites would be affected by invisible internal strain resulting from the layers with different connectivity of ceramics and polymer. Therefore, the internal strain (η) of the composites with different connectivity was calculated to confirm the effects of η on the $\tan \delta$ from the viewpoint of the extrinsic aspect using equation (1) [8]

$$\beta = 2\eta \tan \theta \tag{1}$$

where β is the full-width at half-maximum of the X-ray powder diffraction peaks, η is the internal strain. The β versus $\tan \theta$ was plotted for the composites with different connectivity. The η values were obtained from the slope of the solid line by applying a least squares fit to the data points.

Dependence of the dielectric constant (K) and dielectric loss ($\tan \delta$) of 0.2 V_f ZnMoO₄/PTFE composites on the number of connectivity (Fig.3 (a)) and internal strain (Fig.3 (b)) were investigated as a function of connectivity patterns. With increasing number of connectivity, the K of the composites increased. Especially, the K of the composites was remarkably increased by the connectivity of the ceramics, more so than by the polymer. These results could be attributed to the increase of dipole-dipole interaction with the connectivity of the ceramic particles [9]. The composites with 2 connectivity (0–2, 2–2) of the polymer showed lower η than the composites with 3 connectivity (0–3, 3–3) of the polymer. For the 0.2 V_f ZnMoO₄/PTFE composites with different connectivities, the $\tan \delta$ was dependent on the η values of the composites, as shown in Fig.3 (b).

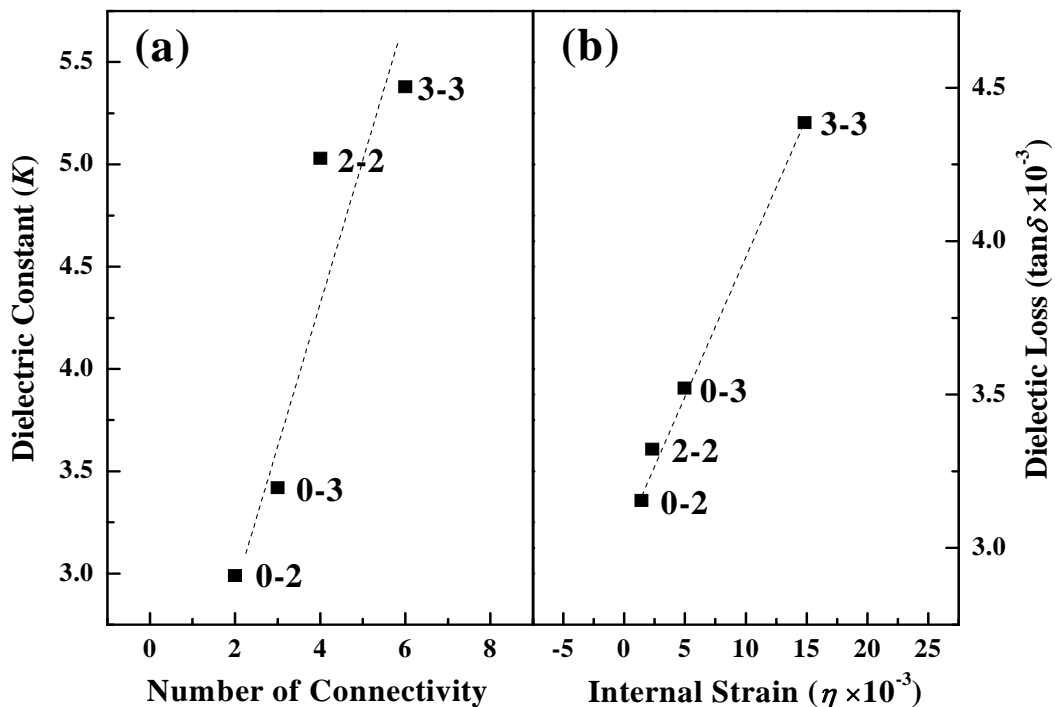


Figure 3. Dependence of the dielectric constant (K) and dielectric loss ($\tan \delta$) of 0.2 V_f ZnMoO₄/PTFE composites on the number of connectivity (a) and internal strain (b).

3.2 Effect of multi-layered structures on the microwave dielectric properties of composite

It was confirmed that there was no reactions between the ceramics (MgMoO₄ (MM) and MgTa₂O₆ (MT)) and PTFE from the XRD patterns, and any cracks, de-bonding, and diffusion between the MM / PTFE layer and MT / PTFE layer were not observed by the SEM micrographs. For the composite with multi-layered structures (Fig.1 (b)), the dielectric properties (K and $\tan\delta$) could be affected by the strains developed from each layer if each layer has different elastic or thermal properties [3].

Table 1 lists the strains (ε) and the strain differences ($\Delta\varepsilon$) between the MT and MM / PTFE layers of the multi-layered 2-2 type composites with 0.2 V_f ceramics. Strain is defined as $\ln(L(T)/L_o)$, where L_o is the initial length, and $L(T)$ is the length of the specimen heated at 300 °C [10]. Strain did not change significantly with the type of multi-layered structure between the MT / PTFE composites. However, the strains of the MM / PTFE composites were dependent on the type of multi-layered structure. The MT / PTFE composites showed greater strains than the MM / PTFE composites. The strain differences of composites decreased with increasing number of layers; it was affected by the array of the layers.

Multi-layered structures	$\varepsilon (\times 10^{-4})$		$\Delta\varepsilon$ (MM-MT) ($\times 10^{-4}$)
	MT	MM	
Double layer	-229	-175	54
Triple layer A (MT/MM/MT)	-243	-175	68
Triple layer B (MM/MT/MM)	-263	-236	27

Table 1. Strain (ε) and strain difference ($\Delta\varepsilon$) between MgTa₂O₆ (MT) and MgMoO₄ (MM) / PTFE layers of composite with multi-layered structures (0.2 V_f ceramics).

Figure 4 shows the dielectric losses ($\tan\delta$) of the 0-3 composites. Increasing ceramic content in the MT / PTFE composites decreased $\tan\delta$ due to MgTa₂O₆ (6.02×10^{-5}) [11] having a lower $\tan\delta$ than PTFE (5.18×10^{-3}) [12] above 10 GHz. The $\tan\delta$ of the MM / PTFE composites decreased up to 0.2 V_f ceramic, it then increased due to lower relative density than 90%. The composites with 0.2 V_f ceramic had highest $\tan\delta$ in the mixed composites (with MT and MM) due to the non-uniform dispersion of ceramics with different particle sizes. The multi-layered 2-2 type composites with 0.2 V_f ceramic affected their $\tan\delta$. These results are explicable through the strain differences of multi-layered composites (Table 1).

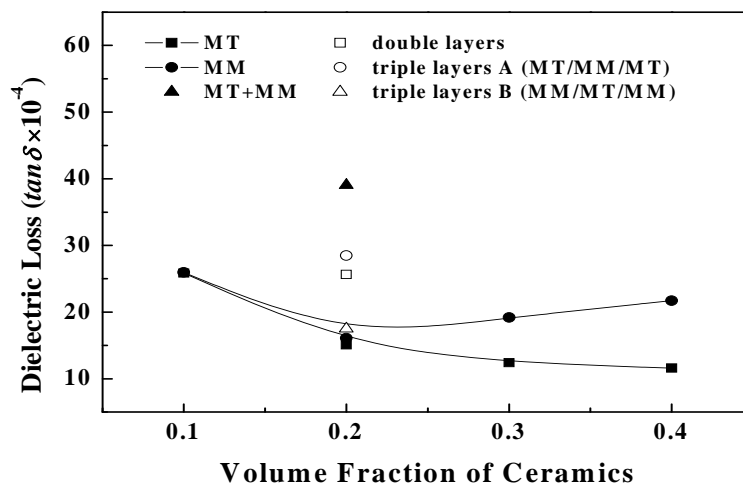


Figure 4. Dielectric loss ($\tan\delta$) of MgTa₂O₆ (MT) and/or MgMoO₄ (MM) / PTFE composites with various volume fractions (V_f) of ceramics and composite with multilayered structures (0.2 V_f ceramics).

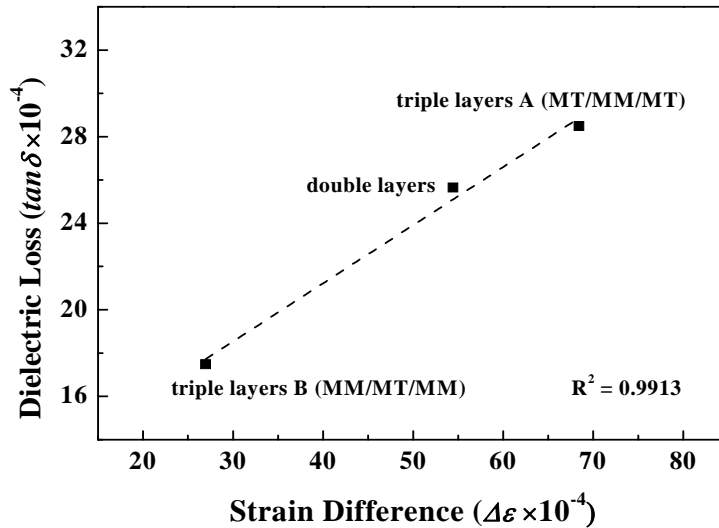


Figure 5. Dependence of dielectric loss ($\tan\delta$) on strain difference ($\Delta\epsilon$) between MgTa_2O_6 (MT) and MgMoO_4 (MM) / PTFE layers of composite with multilayered structures ($0.2 V_f$ ceramics).

The composites with multi-layered 2-2 type composites with $0.2 V_f$ ceramic showed increasing $\tan\delta$ with increasing $\Delta\epsilon$ (Fig. 5).

Dielectric constants (K) of the 0-3 type composites increased with increasing ceramic content (Fig. 6). The MT / PTFE composites showed higher K than the MM / PTFE composites at a given ceramic content. These results are due to the differences in K between the individual components ($\text{MgTa}_2\text{O}_6 = 25.48$, $\text{MgMoO}_4 = 7.05$, PTFE = 2.81). The mixed and multi-layered composites with $0.2 V_f$ ceramic (Fig. 6(b)) had similar dielectric constants. K depended on ceramic content rather than multi-layered structure.

Prediction of effective dielectric constant (K) of a composite from its K and V_f is important in the effective design of ceramic / polymer composites for the applications of electronic packaging and substrates. In addition to the ceramic filler's V_f and K , a dielectric constant (K)

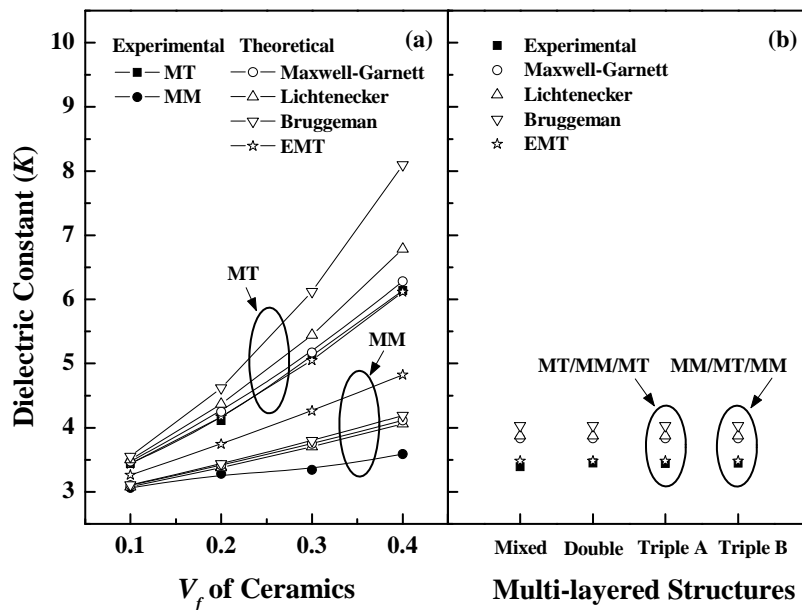


Figure 6. Comparison of theoretical and experimental dielectric constant (K) of MgTa_2O_6 (MT) and/or MgMoO_4 (MM) / PTFE composites with various volume fractions (V_f) of ceramics (a) and composite with multi-layered structures ($0.2 V_f$ ceramics) (b).

of composite is also generally affected by the distribution, shape and size of the ceramic filler and the interfacial interactions (adhesion, porosity and interfacial polarization) between the polymer matrix and the ceramic fillers. [13]. Combining all the necessary parameters into a single equation is difficult. Many theoretical models have been developed to describe an effective K of composites when the filler is variously shaped, sized and distributed. Several theoretical models (such as those of Maxwell-Garnett [14], Lichtenecker [15], Bruggeman [16]) were employed to predict the effective K of the composites (Fig. 6(a)). However, most of the models are valid only for low filler contents (up to 0.1 V_f), because they do not consider interfacial interactions between the polymer matrix and the ceramic filler. The shape and size of the filler and the interfacial interactions between it and the polymer matrix should be considered along with the filler's V_f and K values. The effective medium theory (EMT) model does this, making it suitable for predicting the effective K of composites with small ceramic particle sizes [15]. Experimentally determined K values of the MT / PTFE composites were in good agreement with those predicted by the EMT model (Fig. 6(a)). However, this model was not suitable for the MM / PTFE composites due to their large MM particles. The Lichtenecker model better described the MM / PTFE composites up to 0.2 V_f ceramic, above which the model failed due to low relative density of the composites. All types of multi-layered composites with 0.2 V_f ceramic showed similar K values that were predictable by the EMT model (Fig. 6(b)).

4. Conclusions

The 0–3 type composites of polytetrafluoroethylene (PTFE) with ceramic fillers of different compositions of $ZnMoO_4$, $MgMoO_4$ and $MgTa_2O_6$ showed dielectric constants (K), dielectric losses ($\tan\delta$) that were dependent on their composition and the dielectric properties of the individual components. For the composites with 0.2 V_f of $ZnMoO_4$, the K increased with the connectivity of $ZnMoO_4$ and the composites with 2 (0–2, 2–2) connectivity of PTFE showed lower values of $\tan\delta$ than the composites with 3 (0–3, 3–3) connectivity of PTFE. These results could be attributed to the internal strain with the connectivity patterns.

The $\tan\delta$ of multi-layered 2-2 type composites were affected by strain differences between the $MgMoO_4$ / PTFE and the $MgTa_2O_6$ / PTFE layers. Comparing to the multi-layered 2-2 type composites, the mixed 0-3 composites (with $MgMoO_4$ and $MgTa_2O_6$) showed the highest $\tan\delta$ due to the porosity caused by the inhomogeneous dispersion of variously sized ceramic particles. The dielectric constants of composites depended more on the ceramic content than the multi-layered structure. Dielectric constants of the $MgTa_2O_6$ / PTFE composites were described well by the EMT model. Low loss was obtained in the multi-layered 2-2 type composites with 3 layers (middle $MgTa_2O_6$).

Acknowledgements

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