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Microwave dielectric properties of PTFE/CaTiO$_3$ polymer ceramic composites

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Abstract

CaTiO$_3$ ceramic powder filled polytetrafluoroethylene (PTFE) composites with various filler volume fractions up to 60 vol.% were prepared. The effects of volume fraction of the ceramic filler on the microstructure and microwave dielectric properties of the composites were investigated in detail. As the volume fraction of the ceramic filler increases, the dielectric constant (ε_r) and the temperature coefficient of resonant frequency (τ_f) of composites increase, while the product of quality factor and frequency ($Q \times f$) decreases. Composites with 40 vol.% CaTiO$_3$ exhibited good microwave dielectric properties: $\varepsilon_r = 13$ at ~5 GHz, $Q \times f = 930$ GHz, and $\tau_f = 260$ ppm/°C. Different mixing rules were used to predict the dielectric constant of composites, and it was found that the dielectric constants predicted by Effective Medium Theory (EMT) were in good agreement with experimental data.

Keywords: A. Mixing; B. Composites; C. Dielectric properties

1. Introduction

Ceramic filled polymer composites are finding increasing applications in electronic and microwave devices, since they combine ceramic's electrical properties and the mechanical flexibility, chemical stability, and processing possibility of polymers [1–3]. Polymer ceramic composites with low relative dielectric constant ($\varepsilon_r < 10$) and high quality factor (Q), on one hand, are needed as substrates for microwave frequency uses, since low ε_r is helpful to obtain high transmission speed of the microwave signal. On the other hand, composites with high ε_r (>10) and high Q are needed for the miniaturization of microwave devices and for other cases, for example, the core layers of dielectric waveguides [4]. However few studies are reported on polymer ceramic composites with high ε_r and high Q, and the development of them is one of major challenges in electronic industry. One method to resolve this problem is to use high ε_r ceramic filler with high Q [3,5].

Polytetrafluoroethylene (PTFE) is extensively used as matrix polymer in microwave dielectric composites. PTFE exhibits extremely high Q ($>10^4$), a low and stable ε_r (~2.1) over a wide range of frequency, high melting point (~327 °C), and thermal degradation resistance, all of which make itself ideal choice for fabrication of electronic and microwave devices. However PTFEs high thermal expansion coefficient and low mechanical strength limit its application. In order to improve PTFEs thermal, mechanical, and/or microwave dielectric properties, different ceramic powder fillers with high Q were reported to incorporate into PTFE matrix. These ceramic fillers fall into two groups based on their ε_r values: low ε_r filler ($\varepsilon_r < 20$), including SiO$_2$, Al$_2$O$_3$, MgO, ZnAl$_2$O$_4$–TiO$_2$, TeO$_2$, CeO$_2$, and high ε_r filler ($\varepsilon_r > 20$), including BZN, TiO$_2$, Sr$_2$Ce$_2$Ti$_5$O$_{16}$ [6–14].

The present paper aimed to obtain ceramic filled composites with high ε_r and high Q using CaTiO$_3$ as filler and PTFE as matrix. CaTiO$_3$ is of very high ε_r and high Q at microwave frequency ($\varepsilon_r = 162$ and $Q = 8700$ @1.49 GHz) [15]. The microstructure and microwave dielectric properties of PTFE/CaTiO$_3$ composites with CaTiO$_3$ volume fraction in the range of 0–60 vol.% were investigated in detail. Composites with 40 vol.% CaTiO$_3$ exhibited good microwave dielectric

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properties: $\varepsilon_r = 13$, product of quality factor and frequency $Q \times f = 930$ GHz, and temperature coefficient of resonant frequency $\tau_f = 260$ ppm/°C.

2. Experimental

$CaTiO_3$ ceramic powder was synthesized by solid state reaction route. Starting reagents $CaCO_3$ (AR purity) and TiO_2 (AR purity) were weighed in stoichiometric ratio, mixed with de-ionized water using a planetary ball mill, dried, and then calcinated in a muffle oven at 1310 °C for 2 h. The calcinated mixture was ground with de-ionized water using a planetary ball mill for 2 h, and dried. And pale purple $CaTiO_3$ ceramic powder was obtained. The phase formation of $CaTiO_3$ was confirmed by X-ray diffraction (XRD).

PTFE/$CaTiO_3$ composites were prepared by mold pressing and heating the mixture of PTFE and $CaTiO_3$. Different volume fractions (0–60 vol.%) of $CaTiO_3$ powder and starting PTFE powder (particle size 20–70 μm, Chenguang Research Institute of Chemical Industry, China) were dispersed in ethyl alcohol using an ultrasonic mixer for about 30 min. Dry powder mixtures were obtained by removing the solvent at 70 °C under stirring. Then the mixtures were mold pressed into cylinder samples of 25 mm in diameter and ~22 mm in height at pressure of 240 MPa. Finally the compact samples were heated to 360 °C at a rate of 200 °C/h and soaked for 2 h.

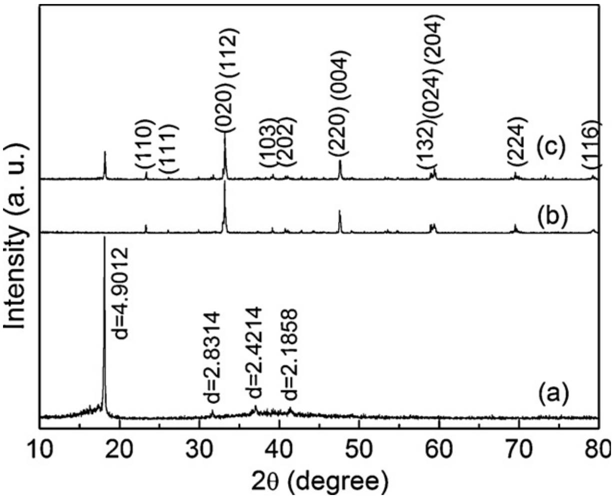

Fig. 1. XRD patterns of (a) PTFE/$CaTiO_3$ composite with 0 vol.% of $CaTiO_3$, (b) synthesized $CaTiO_3$ powder, and (c) composite with 40 vol.% of $CaTiO_3$.

XRD patterns were carried out on a D8 Advance X-ray Diffractometer (Bruker AXS) with Cu Kα irradiation. Scanning electron microscopy (SEM) images were collected with JSM-5610 LV (JEOL). The bulk densities of samples were measured by Archimedes method. ε_r and $Q \times f$ were measured using a silver cavity ca. 4 times the diameter of the test resonator (this ensured an isolated but shielded resonator) and an Advantest network analyzer operating in the $TE_{01\delta}$ resonance mode in

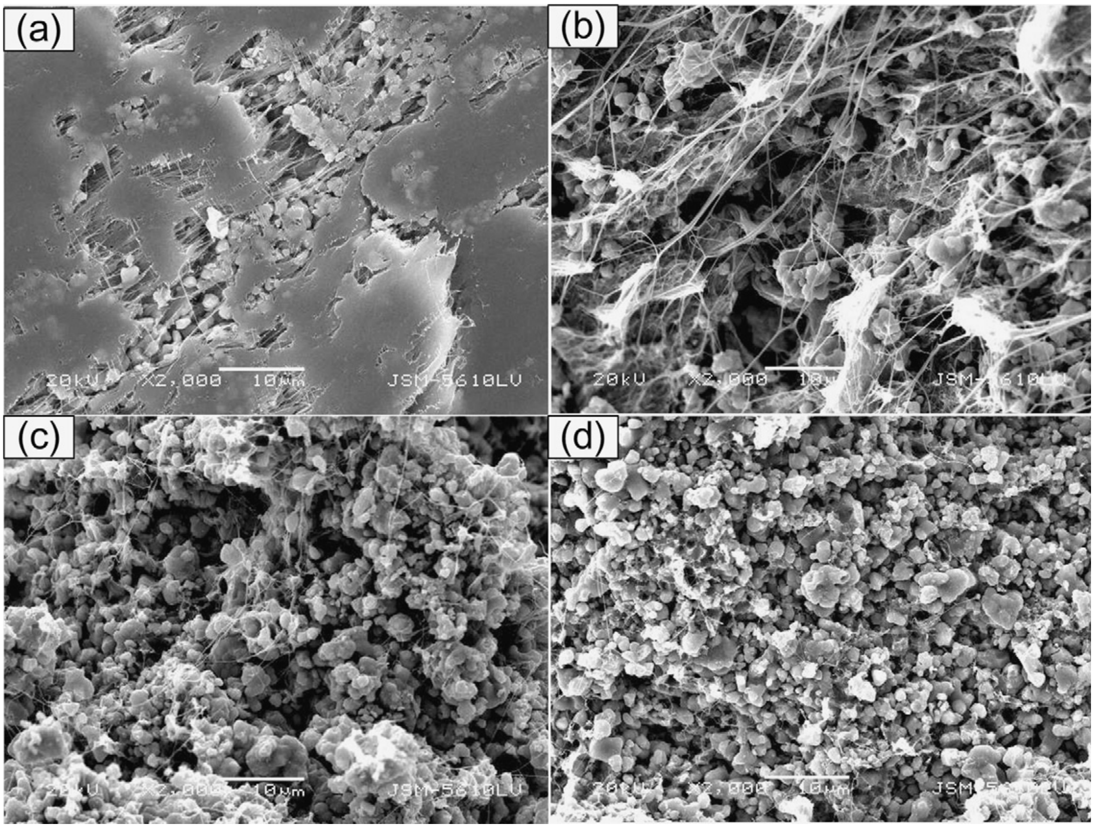

Fig. 2. (a) Planar SEM image of PTFE/$CaTiO_3$ composite with 10 vol.% of $CaTiO_3$. (b)–(d) cross-sectional SEM images of PTFE/$CaTiO_3$ composites with 10 vol.%, 30 vol.%, and 60 vol.% of $CaTiO_3$, respectively.

reflectance [16,17]. The resonant frequencies for samples were found in the range of 2.0–7.5 GHz. For the measurement of τ_f, the technique is the same as that of $Q \times f$ measurement. The test cavity was placed over a thermostat and the temperature range used was from 30 to 80 °C. The τ_f values were calculated as follows:

$$\tau_f = \frac{(f_{80} - f_{30}) \times 10^6}{(80 - 30) f_{30}} (\text{ppm}/^\circ\text{C}), \quad (1)$$

where f_{80} and f_{30} are the resonant frequencies at 80 and 30 °C, respectively.

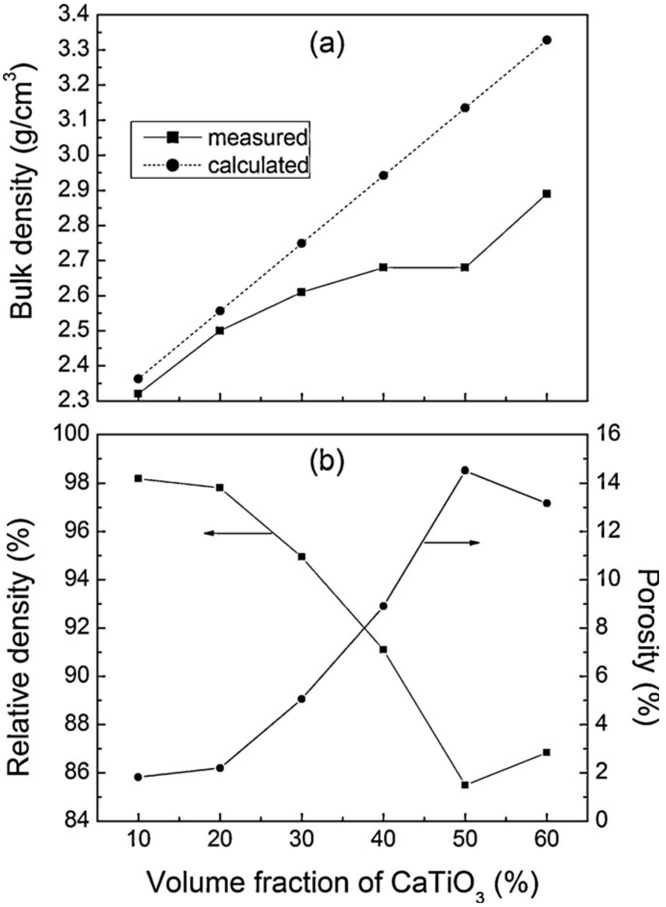

Fig. 3. (a) Measured and calculated bulk density of composites at different volume fractions of CaTiO$_3$. (b) Relative density and calculated porosity of composites at different volume fractions of CaTiO$_3$.

3. Results and discussion

Fig. 1c gives the XRD pattern of a PTFE/CaTiO$_3$ composite sample with 40 vol.% of CaTiO$_3$. For comparison, Fig. 1a and b give the XRD patterns of the composite with 0 vol.% of CaTiO$_3$ (pure PTFE) and the synthesized CaTiO$_3$ powder. Fig. 1a indicates that after heated at 360 °C, the PTFE compact without CaTiO$_3$ is of crystalline PTFE structure (JCPDS 47-2217). Fig. 1b indicates that the synthesized CaTiO$_3$ powder is of orthorhombic perovskite structure (JCPDS 86-1393), and that no CaO, CaCO$_3$, or TiO$_2$ phase is detected. The XRD peaks of the composite with 40 vol.% ceramic filler (Fig. 1c) can be indexed based on JCPDS 47-2217 and 86-1393, indicating that the composite is a mixture of PTFE and CaTiO$_3$.

In Fig. 2 are shown the SEM images of PTFE/CaTiO$_3$ composites with different volume fractions of the ceramic filler. It can be seen from Fig. 2 that CaTiO$_3$ particles are of sphere-like shape with an average size of ca. 3 μm. At lower volume fraction (10 vol.%, Fig. 2a and b), CaTiO$_3$ particles disperse well in PTFE matrix, indicating that the ceramic filler is compatible with the matrix. At higher volume fractions (>30 vol.%, Fig. 2c and d), most ceramic particles connect one another. In addition, pores exist in composite samples in the volume fraction range of 10–60 vol.%.

Fig. 3a shows the variation in the measured and calculated values of the bulk density of PTFE/CaTiO$_3$ composites with the volume fraction of CaTiO$_3$. The calculated values of the bulk density of composites, ρ_{cal}, are obtained using equation

$$\rho_{cal} = \rho_f V + \rho_m (1 - V), \quad (2)$$

where ρ_f and ρ_m are the density of the filler and the matrix, respectively, and V is the volume fraction of the filler. Obviously ρ_{cal} increases linearly with increasing V since the density of CaTiO$_3$ (ρ_f = 4.1 g/cm^3) is higher than that of PTFE (ρ_m = 2.2 g/cm^3). However the measured bulk density exhibits a non-linear increase with increasing volume fraction of the filler and especially stays almost unchanged in the range of 40–50 vol.%. Furthermore the measured density is smaller than calculated one at fixed volume fraction of the filler, which may result from the presence of pores in composites. The deviation of the measured density from the calculated one increases with increasing volume fraction of the filler. The porosity, p, of composites can be calculated from the measured and calculated density of composites using equation

$$\rho_{mea} = \rho_f V(1 - p) + \rho_m (1 - V)(1 - p) + \rho_{pore} p, \quad (3)$$

where ρ_{mea} and ρ_{pore} are the measured density of composites and the density of pores in composites, respectively. Since ρ_{pore} is very small, item $\rho_{pore}p$ in Eq. (3) can be omitted, and from Eqs. (2) and (3) we have

$$p = 1 - \frac{\rho_{mea}}{\rho_{cal}} = 1 - \rho_{rel}, \quad (4)$$

where ρ_{rel} is the relative density of composites. The dependences of the relative density and the porosity of composites on the volume fraction of the filler are shown in Fig. 3b. The relative density (porosity) of PTFE/CaTiO$_3$ composites decreases (increases) as the volume fraction of the CaTiO$_3$ filler increases from 10 to 50 vol.%, indicating the increase in void formation inside the composite at higher volume fraction of the filler. At higher volume fraction of the filler, the porosity of PTFE/CaTiO$_3$ composite (∼9% at 40 vol.%) is much smaller than that of PTFE/CeO$_2$ (∼22% at 40 vol.%) and POE/SrTiO$_3$ (∼19% at 40 vol.%) [5,10], and this may be due to the good compatibility between PTFE and CaTiO$_3$. However the relative density (porosity) of PTFE/CaTiO$_3$ composites slightly increases (decreases) as the volume fraction of the filler

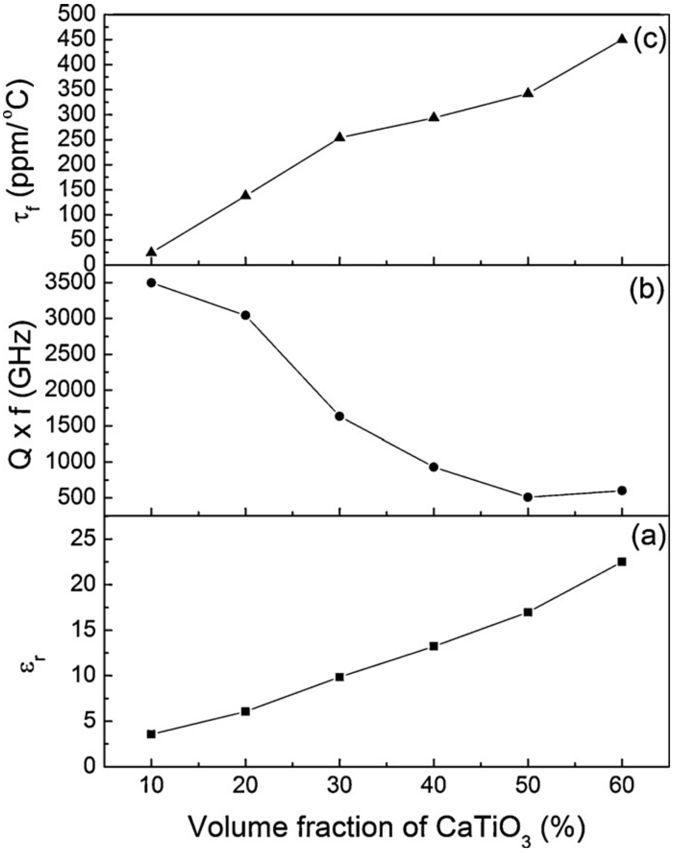

Fig. 4. Microwave dielectric properties of PTFE/$CaTiO_3$ composites: (a) ε_r, (b) $Q \times f$, and (c) τ_f as a function of volume fraction of the $CaTiO_3$ filler.

increases from 50 to 60 vol.%, indicating the inhibition of void formation inside the composite in which the ceramic dominates in volume over PTFE.

Fig. 4 gives microwave dielectric properties of PTFE/$CaTiO_3$ composites as a function of volume fraction of the $CaTiO_3$ filler. The dielectric constant of the composite increases with increasing volume fraction of the filler, from 3.6 at 10 vol.% to 22.5 at 60 vol.% (Fig. 4a), since the dielectric constant of the $CaTiO_3$ filler is much higher than that of the PTFE matrix. A number of numerical relations have been put forward to predict the dielectric constant of composites. Herein the following equations are used to calculate the dielectric constants of PTFE/$CaTiO_3$ composites:

$$\ln \varepsilon_r = V \ln \varepsilon_f + (1 - V) \ln \varepsilon_m, \tag{5}$$

$$\varepsilon_r = \frac{\varepsilon_m(1-V) + \varepsilon_f V[(3\varepsilon_m)/(\varepsilon_f + 2\varepsilon_m)] \times [1 + ((3V(\varepsilon_f - \varepsilon_m))/(\varepsilon_f + 2\varepsilon_m))]}{(1-V) + V[(3\varepsilon_m)/(\varepsilon_f + 2\varepsilon_m)] \times [1 + ((3V(\varepsilon_f - \varepsilon_m))/(\varepsilon_f + 2\varepsilon_m))]}, \tag{6}$$

$$\frac{\varepsilon_r - \varepsilon_m}{\varepsilon_r + 2\varepsilon_m} = V \frac{\varepsilon_f - \varepsilon_m}{\varepsilon_f + 2\varepsilon_m}, \tag{7}$$

$$\varepsilon_r = \varepsilon_m \left[1 + \frac{V(\varepsilon_f - \varepsilon_m)}{\varepsilon_m + n(1-V)(\varepsilon_f - \varepsilon_m)}\right]. \tag{8}$$

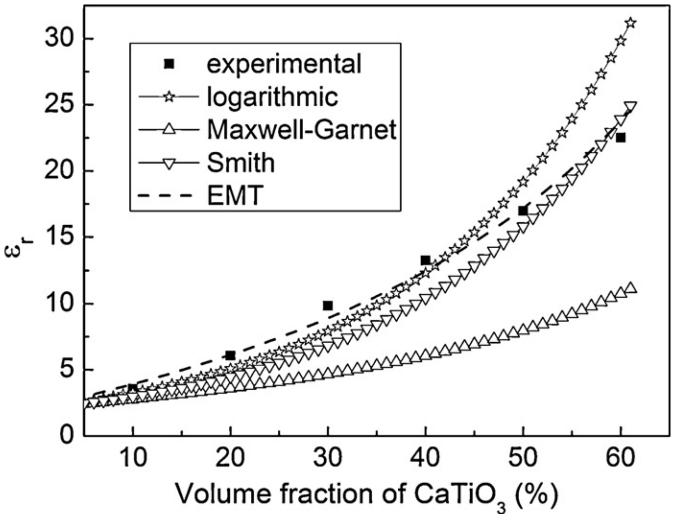

Fig. 5. Comparison of experimental data and calculated values with different models for dielectric constant of PTFE/$CaTiO_3$ composites.

Eqs. (5)–(8) are the expressions of logarithmic, Smith's, Maxwell-Garnet's, and Effective Medium Theory (EMT) mixing rules, respectively [18–20], where ε_r, ε_f, and ε_m are the dielectric constant of PTFE/$CaTiO_3$ composites, the $CaTiO_3$ filler ($\varepsilon_f = 162$), and the PTFE matrix ($\varepsilon_m = 2.1$), respectively, and n is the shape factor of the filler. Fig. 5 shows the comparisons of the dielectric constants of PTFE/$CaTiO_3$ composites with the values predicted by the above equations. It can be seen that in the lower volume fraction region the predicted values by the four mixing rules match well with the experimental data, and as the volume fraction increases, the predicted values by the logarithmic, Smith's, and Maxwell-Garnet's mixing rule deviate from the experimental data. For the EMT mixing rule, the relative deviation between predicted values and experimental data is less than 10% in the volume fraction range of 0–60 vol.%, and $n = 0.115$. This shape factor value is very small, indicating that the filler particles are of sphere shape [21], which is in good agreement with SEM observation. Therefore the EMT can predict well the dielectric constant of PTFE/$CaTiO_3$ composites.

The $Q \times f$ value of PTFE/$CaTiO_3$ composites decreases with increasing volume fraction of the $CaTiO_3$ filler in composites (Fig. 4b), although each of the filler and the matrix has a very high Q value. The $Q \times f$ value of composites is affected by many factors such as porosity, and interface between the two components in the composite. The interface between PTFE and $CaTiO_3$ in PTFE/$CaTiO_3$ composites increases as the volume fraction of the ceramic increases. The decrease in the $Q \times f$ value of PTFE/$CaTiO_3$ composites with the volume fraction of the filler is attributed to the increased interfacial polarization at higher volume fraction of the ceramic filler.

Fig. 4c gives the variation in the τ_f value of the PTFE/$CaTiO_3$ composites with the volume fraction of the ceramic filler. It can be seen that the τ_f value of the PTFE/$CaTiO_3$ composites increases with increasing volume fraction of the $CaTiO_3$ filler, from 25 ppm/°C at 10 vol.% to 450 ppm/°C at

60 vol.%. This variation tendency can be roughly estimated by the simple mixing rule using the τ_f values of PTFE and $CaTiO_3$ at microwave frequency (−25 and 860 ppm/°C [15,22], respectively).

4. Conclusions

PTFE/$CaTiO_3$ polymer ceramic composites were prepared by powder processing technique for microwave frequency application. XRD patterns indicate that the composites consist of crystalline PTFE (JCPDS 47-2217) and orthorhombic perovskite $CaTiO_3$ (JCPDS 86-1393). At lower volume fraction of $CaTiO_3$, ceramic particles disperse well in the PTFE matrix, while the packing of ceramic particles grew denser with the increase in the filler content. The dielectric constant and the τ_f value of composites increased, while the $Q \times f$ value decreased with increasing volume fraction of $CaTiO_3$ in composites. Composites with 40 vol.% $CaTiO_3$ are of high ε_r and high Q: $\varepsilon_r = 13$, $Q \times f = 930$ GHz, and $\tau_f = 260$ ppm/°C. The prediction of the dielectric constant of PTFE/$CaTiO_3$ composites using EMT is in good agreement with the experimental data.

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