Effects of CaTiO₃ Loading on the Properties of PTFE/TiO₂ Composites

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Abstract
In this paper, a detailed study was carried out on the PTFE reinforced with TiO₂ and CaTiO₃. The filler content of ceramic powder was a fixed value of 61 wt% and the content of CaTiO₃ in PTFE matrix varied from 0 wt% to 16 wt% with a step size of 4 wt%. The effects of CaTiO₃ loading on the density, moisture absorption, thermal expansion, microstructure and microwave dielectric properties were investigated. As CaTiO₃ loading content increased from 0 wt% to 16 wt%, the thermal expansion initially displayed a sharp increase, and showed a slight enhancement when the content of CaTiO₃ exceeded 12 wt%. The density experienced a continuous decrease with the addition of CaTiO₃. The moisture absorption displayed a steady increase with the increasing CaTiO₃ loading amount. The changing of dielectric constant (εᵣ) and loss tangent (tanδ) were similar to that of the moisture absorption in a manner. Good dielectric properties with values of εᵣ = 11.60, tanδ = 0.002 were obtained in the PTFE matrix with 16 wt% CaTiO₃ and 45 wt% TiO₂.

Keywords
Composites, TiO₂, PTFE, CaTiO₃, Dielectric Properties

1. Introduction
Ceramic powder filled polytetrafluoroethylene (PTFE) has been widely studied in fabrication of microwave devices because of its very low loss tangent and excellent chemical resistance. PTFE is a kind of high performance high performance thermoplastic polymer with excellent electrical properties. It has a low dielectric constant (εᵣ = 2.1) and an extremely low loss tangent (tanδ = 0.0003) which are stable over a wide range of frequencies [1]. However, the disadvantages of PTFE are its high linear coefficient of thermal expansion (CTE = 109 ppm·°C⁻¹) and low mechanical strength. One of the methods to control the CTE
and mechanical strength of PTFE was to add inorganic ceramic fillers into the PTFE matrix [2] [3] [4] [5]. In previous work, several researches have investigated the effects of ceramic filler materials, such as TiO₂ [6], MgTiO₃ [1], CaTiO₃ [7], etc.

It is well known that both the microwave dielectric properties and the thermal expansion of substrate composites are very important factors for the fabrication of microwave circuit. The object of this work is to study the effect of CaTiO₃ loading on the properties of TiO₂ filled PTFE composites, such as density, moisture absorption, thermal expansion, microstructure and microwave dielectric properties. CaTiO₃ and TiO₂ powders were prepared by conventional solid-state reaction technique. The total content of inorganic ceramic fillers was a fixed value of 61 wt%, and the content of CaTiO₃ in PTFE/TiO₂ matrix varied from 0 wt% to 16 wt% with a step size of 4 wt%. The effects of CaTiO₃ loading on the properties of PTFE/TiO₂ composites have been investigated systematically. It is expected that this work will be useful in the applications of TiO₂/PTFE substrate composites in practice.

2. Experimental Procedures

2.1. Materials

The raw materials used were rutile TiO₂ powder, CaTiO₃ and PTFE aqueous dispersion (TE-3865C, Dupont, USA). Phenyltrimethoxysilane (PTMS, TCI Corporation, Japan) was used as silane coupling agent. The average size of rutile TiO₂ and CaTiO₃ powders were 5 μm and 2 μm, respectively. The values of D50 were measured by Laser particle size analyzer. Table 1 gives the properties of raw materials.

| Properties              | PTFE | TiO₂ | CaTiO₃ |
|-------------------------|------|------|--------|
| Density/(g/cm³)         | 2.2  | 4.0  | 4.0    |
| Dielectric constant     | 2.1  | 90   | 140    |
| Dielectric loss         | 0.0003 | 0.008 | 0.0006 |
| Thermal expansion coefficient/(10⁻⁶K⁻¹) | 109 | 9    | 9      |

2.2. Fabrication of the Composite

Phenyltrimethoxysilane (PTMS) was used to coat the surface of filler particles as coupling agent. First, PTMS was hydrolyzed in alcohol and deionized water for 1 h at 55°C. The amount of PTMS was 1.5% of the weight of ceramic filler and the amount of water was controlled exactly for the hydrolysis of PTMS. Then CaTiO₃ and TiO₂ were added and dispersed into the hydrolyzed coupling agent solution by heavy stirring for 2 h. The product was further dried in an oven at 120°C for 3 h and silane coupling agent treated ceramic powder was obtained.
After drying, the ceramic powder previously obtained was weight accurately to prepare the composites according to the weight ratio of $x \text{CaTiO}_3(61-x)\text{TiO}_2/39\text{PTFE}$ ($x = 0, 4, 8, 12, 16$). The coupling agent treated ceramic powder was added into the aqueous PTFE matrix and mixed by heavy stirring for 3 h to obtain good slurry. The slurry was then dried at 120°C for 24 h to remove water. The dried dough was smashed by a high speed milling. The obtained composite powder was pressed into square slices with length of 30 mm, width of 20 mm and height of 1 mm by cold pressing under a pressure of 20 MPa. The slices were hot pressing sintered at 360°C and 10 Mpa. Hot treatment was performed in a program controlled oven. PTFE was melted and coalesced during hot treating, and then recrystallized while cooling.

### 2.3. Characterization Studies

Archimedes’ principle was used to study the density of the PTFE reinforced with TiO$_2$ and CaTiO$_3$ composites. The microstructure of the substrate was observed by scanning electron microscopy (SEM, model JEOL JSM-6490). Water absorption of the composite sample was measured as reported earlier by Murali etc [2]. Netzsch DIL402PC was used to measure the coefficient of thermal expansion (CTE) of the substrate composites.

The dielectric constant ($\varepsilon_r$) and dielectric loss (tan$\delta$) of CaTiO$_3$/TiO$_2$-filled PTFE composites were measured by stripline resonator method using Agilent E8363A microwave network analyzer according to IPC-TM-650 2.5.5.5 specification. The testing sizes of samples were 30 mm long, 20 mm wide and 1 mm thick. The testing frequencies varied from 7.0 GHz to 13.0 GHz. The $\varepsilon_r$ and tan$\delta$ of the CaTiO$_3$/TiO$_2$-filled PTFE composites reported in this paper was at a frequency about 10 GHz.

### 3. Results and Discussion

#### 3.1. Density Tests

Variation of the theoretical density and bulk density of TiO$_2$/CaTiO$_3$ co-filled composites with CaTiO$_3$ loading is shown in Figure 1. A comparison of experimental results with theoretical values is also presented in Figure 1. It is difficult for PTFE to have strong adhesion with ceramic powder as PTFE has a low surface energy. Experimental results are always lesser than theoretical values because of the generating of pores at the interface region of matrix, which would decrease the density of the composite. With increasing CaTiO$_3$ addition, the relative density of the substrate displayed a continuous decrease. Obviously, with the CaTiO$_3$ loading amount increased to 16 wt%, the density reached the minimum value of 2.99 g/cm$^3$. In our previous study [7], it is true that interface volume fraction increases with decreasing ceramic particle size, which promotes porosity factor of the substrate. This is because the ceramic powders trend to agglomerate with the decrease of particle size, and the bad dispersion in the PTFE matrix which produces more pores in the matrix and decreases the density.
Figure 1. Variation of the theoretical density and bulk density of TiO₂/CaTiO₃ co-filled composites with CaTiO₃ loading.

Figure 2. Variation of water absorption with respect to CaTiO₃ loading.

3.2. Water Absorption

It is well known that water absorption is an important parameter to control for the practical use of substrate composites. Previous studies showed that the moisture absorption of substrate composite was strongly influenced by the hydrophilic nature of ceramic filler and porosity factor of substrate. Figure 2 shows the variation of water absorption of CaTiO₃/TiO₂-filled PTFE composites with respect to CaTiO₃ filler loading. Since modified CaTiO₃, TiO₂ powder and PTFE are hydrophilic, the moisture of the composite was mainly determined by the porosity factor of the matrix. As shown in Figure 2, the water absorption displayed a continuous increase with the addition of CaTiO₃ loading amount. This finding probably was related to more pores generating at the interface region, leading to the deterioration of moisture absorption.
3.3. Thermal Expansion Property

In addition to dielectric properties, the coefficient of thermal expansion of the substrate is also very important for the application of the composite. The composite must have a low value of CTE in order to match with the CTE of copper conductor layer. Variation of CTE of CaTiO$_3$/TiO$_2$ co-filled composites with respect to CaTiO$_3$ loading amount is shown in Figure 3. As CaTiO$_3$ loading amount increased from 0 wt% to 16 wt% with step size of 4 wt%, the thermal expansion initially displayed a sharp increase, later a slight climb when the content of CaTiO$_3$ was 12 wt%.

3.4. Morphology Aspects

Morphology and the dispersion of ceramic filler in PTFE matrix were observed using SEM. The cross sectional SEM images of pure TiO$_2$ filled PTFE sample and 16 wt%CaTiO$_3$/TiO$_2$ co-filled sample are shown in Figure 4. It can be seen that all samples exhibit two-phase structure including PTFE and ceramic powder. It is difficult for ceramic powders to have a good adhesion with PTFE because of the low surface energy of PTFE has a low surface energy. Large amounts of pores can be observed in the images. Obviously, as the addition of CaTiO$_3$ loading amount the agglomeration of ceramic filler appeared which deteriorates the porosity factor of samples.

The typical planar SEM micrographs of pure TiO$_2$ filled PTFE sample and 16 wt%CaTiO$_3$/TiO$_2$ co-filled sample are shown in Figure 5. As shown in Figure 5(a), PTFE has a better adhesion with pure TiO$_2$ powder. However, Figure 5(b) shows a terrible bond between ceramic powder and PTFE.

3.5. Dielectric Properties

The dielectric properties of the substrate composites depend on not only the dielectric properties of the components but also other factors such as the interactions between ceramics and polymers, the size of fillers, and the dispersion of

![Figure 3](image)

Figure 3. Coefficient of thermal expansion of TiO$_2$/CaTiO$_3$ co-filled composites.
fillers in polymer matrix [8] [9] [10]. Figure 6 shows the dielectric constant and dielectric loss of the composites as a function of CaTiO$_3$ loading percent. The composite has low loss tangent values (<0.002). As the addition of CaTiO$_3$ loading amount increased, the loss tangent increases sharply at first, and then go up to the maximum values when the loading content of CaTiO$_3$ exceeds 12 wt%. Since water has high loss tangent (tanδ = 35), the dielectric loss of the substrate composites would deteriorate while moisture absorption increases [3]. With increasing CaTiO$_3$ content, the value of dielectric has a tendency of persistent increase. The main reason for this phenomenon is that the dielectric constants of composites are strongly dependent on the relative permittivity of the ceramic components.

4. Conclusion

Rutile TiO$_2$ and CaTiO$_3$ powder were modified and filled in PTFE matrix in fixed ratio of xCaTiO$_3$/(61 − x)TiO$_2$/39PTFE (x = 0, 4, 8, 12, 16) through cold pressing and hot treating process to fabricate TiO$_2$/CaTiO$_3$ co-filled PTFE composites for microwave substrate applications. The effects of CaTiO$_3$ loading amount on the density, moisture absorption, thermal expansion, microstructure and microwave dielectric properties were studied. The density experienced a continuous decrease with the addition of CaTiO$_3$. The moisture absorption displayed a steady increase with the increase of CaTiO$_3$ loading amount.
Figure 6. Variation of dielectric constant and loss tangent at 10 GHz of TiO₂/CaTiO₃ co-filled composites with respect to the content of CaTiO₃.

loading amount increased from 0 wt% to 16 wt%, the thermal expansion displayed a sharp increase at first and then a slight climb when the content of CaTiO₃ was 12 wt%. The changing of dielectric constant (εr) and loss tangent (tanδ) were similar to that of the moisture absorption in a manner. Good dielectric properties with values of εr = 11.60, tanδ = 0.002 were obtained in the PTFE matrix with 16 wt% CaTiO₃ and 45 wt% TiO₂. At last, TiO₂/CaTiO₃ co-filled PTFE composites are promising candidates for microwave circuit applications.

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