Microwave dielectric properties of SrAl$_2$Si$_2$O$_8$ filled Polytetrafluoroethylene composites

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Abstract. The properties of Polytetrafluoroethylene (PTFE) filled with SrAl$_2$Si$_2$O$_8$ (SAS) and alkali-free glass fiber (GF) were investigated. The content of GF is 1 vol. %, and the content of SAS varied form 10 vol. % to 50 vol. %. The SAS was modified by silane coupling agent to improve interaction between SAS and PTFE, and the composites were prepared through SMECH (include Sigma Mixing (SM), Extrusion (E), Calendering (C) and Hot pressing (H) ) process. XRD was used to testify the phase purity of SAS. FTIR was used to analyze the surface of modified SAS. The SAS/PTFE composite material exhibited a near-zero dielectric constant temperature coefficient ($\tau_e=5.1 \text{ ppm}/^\circ\text{C}$) while achieving a low dielectric constant ($\varepsilon_r=3.21$) and a low dielectric loss ($\tan\delta=0.00136$) at 40 vol. % SAS filling. The SAS/PTFE composites are potential candidates for microwave substrates applications.

1. Introduction

Polymer–ceramic composites have aroused much attention in dielectric substrates, microelectronic packages and other electrical applications. Polymers have many advantages over the conventional ceramic substrates, such as low density, low moisture absorption, high chemical resistance and low energy consumption. At the same time, the introduction of ceramics has solved the problems of polymers, such as high coefficient of thermal expansion, poor dimensional stability and low mechanical stiffness [1-4]. The advantages of both the phases were combined by polymer–ceramic composites to obtain excellent dielectric, thermal, and mechanical properties. It is well known that the properties of composites depend on a number of parameters, such as volume fraction of the filler, filler or particle sizes, distributions, individual properties of the components, processing techniques and the interaction between the polymer and filler [5, 6]. It is difficult to combine fillers and polymer due to the significant differences in surface between polymer and ceramic. The difference in surface properties between the polymer and the filler leading to high porosity and moisture absorption resulting in detrimental change in mechanical and dielectric properties. Many coupling agents have been developed to improve the properties of composites, which have two different functional groups, one group is mixed with the polymer and the other is combined with the filler. Meanwhile, the coupling agents covered filler can prevent the agglomeration of filler [7, 8].

Among the various polymers, PTFE plays a vital role due to the excellent superior dielectric properties($\varepsilon_r=2.1$, $\tan\delta=0.0003$), thermostability and superior chemical inertia[9, 10]. In addition, the
dielectric and mechanical properties can be improved by filling ceramic [11-16]. Speed of signal transmission is negatively correlated with $\varepsilon_r$. In order to improve the speed of signal transmission, $\varepsilon_r$ of the filler should be as small as possible. Dielectric loss is closely related to energy loss during signal transmission. In order to reduce the energy loss, low dielectric loss is necessary. Meanwhile, the $\tau_r$ is a pivotal parameter for packaging materials. A slight fluctuation in $\varepsilon_r$ will lead to a shift in the frequency of any devices using such materials[16]. Wang et al.[17] reported that $\text{SrAl}_2\text{Si}_2\text{O}_8$ (SAS) ceramic has a low $\varepsilon_r$ (3.56), a high quality factor $Q \times f = 14590$ GHz and a positive $\tau_r$ (∼60ppm/°C). It allows SAS/PTFE composites for achieving near-zero $\tau_r$ while achieving low $\varepsilon_r$ and low $\tan\delta$.

In this work, the content of GF in composites is a fixed value of 1 vol. % to reduce the linear coefficient of thermal expansion, and the content of SAS was from 10 vol. % to 50 vol. %. The GF and SAS powders were modified by phenyltrimethoxysilane (Z6124) to reduce water absorption by SAS and GF, and improve the interface properties of composites [18, 19]. Consequently, the effects of SAS adding on density, moisture absorption, dielectric properties ($\varepsilon_r$, $\tan\delta$) and temperature coefficient of dielectric constant were investigated for the formulated SAS/PTFE composites.

2. Experimental

2.1. Preparation of SAS powder

The powders of $\text{SrCO}_3$, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ were weighed in stoichiometric proportion of $\text{SrAl}_2\text{Si}_2\text{O}_8$ and ball milled at a speed of 280 rpm for 3 h. The mixture was dried at 120 °C, and then the dried powder was calcined at 1350 °C for 3 h. The calcined powder was ball milled for 1 h to obtain the SAS powders. The properties of SAS, GF and PTFE were showed in Table 1.

| Properties                          | SAS   | GF    | PTFE  |
|-------------------------------------|-------|-------|-------|
| Dielectric constant ($\varepsilon_r$)| 3.56  | 4.9   | 2.1   |
| Dielectric loss ($\tan\delta$)      | 0.0009| 0.006 | 0.0003|
| Density (g/cm$^3$)                  | 3.17  | 2.6   | 2.2   |
| Coefficient of thermal expansion (CTE)(ppm/°C) | 2.3   | 4.8   | 109   |

2.2. Preparation of the composite substrates

First, deionized water was added into beaker and adjust the pH was adjusted with glacial acetic acid, and then SAS powder was dispersed in mixture for 30 min. Z6124 ($\text{C}_x\text{H}_y\text{O}_z\text{Si}$, TCI Corporation, Japan) was added into the mixed solution. After that, the obtained mixture was heated at 120 °C to obtain the SAS powder treated by Z6124. The SAS powder and GF (Huate, Shanxi) composites with PTFE (DISP30, Dupont, China) by high-speed dispersion mixer, then the sheets were prepared by calendaring, and dried at 200 °C. Finally, the dried sheets were hot-pressed with 20 MPa at 370 °C for 2 h, and the dielectric composite substrates were obtained after cold in the hot-press.

2.3. Characterization studies

The brittle fractured cross sectional morphologies of the composites were observed by scanning electron microscopy (microscope model JEOL JSM-6490). The Archimede's theorem was used to measure the density. The moisture absorption of the composites was measured according to IPC-TM-650 2.6.2[20]. The X-ray powder diffraction (XRD) was used to examine the crystal phase. The surface of ceramic was observed through Fourier transform infrared spectra (Nicolet FTIR 5700 spectrophotometer). The $\varepsilon_r$, $\tan\delta$ and $\tau_r$ of the composites were examined according to IPC-TM-650 2.5.5.5 [21]. The $\varepsilon_r$ and $\tan\delta$ were measured at a frequency around 10 GHz, and the $\tau_r$ was measured in the 0-100 °C range.
2.4. Theoretical modeling

The calculated dielectric constant was obtained from Lichtenecker model [2]:
\[ \ln \varepsilon_{\text{eff}} = \nu_f \ln \varepsilon_f + (1 - \nu_f) \ln \varepsilon_m \]  \hspace{1cm} (1)
where the \( \varepsilon_{\text{eff}} \), \( \varepsilon_f \) and \( \varepsilon_m \) represents the dielectric constant of composites, SAS and matrix, respectively. \( \nu_f \) represent the volume fraction of SAS. And the \( \tau_\varepsilon \) was studied using the follow equation [22]:
\[ \tau_\varepsilon = \frac{\varepsilon_r}{3} \left( \frac{1}{\alpha} \times \frac{\partial \alpha}{\partial T} - 3\alpha_t \right) \]  \hspace{1cm} (2)
where the first term represents the change in polarization of composites over temperature, and the second term represents the linear coefficient of thermal expansion (CTE).

3. Results and discussion

3.1. Characterization of modified SAS particles

The structure of ceramic is very important of composites. To confirm the structure of ceramic, the XRD was used to analyze the obtained powder through solid state ceramic route. And the XRD pattern of SAS was shown in Figure 1. The powder diffraction pattern of SAS with monoclinic structure is indexed based on ICDD file card no. 38–1454[17]. As shown in Figure 1, no secondary phases were detected by matching with the standard ICDD file card, meaning that the pure phase SAS with monoclinic structure was prepared.

![Figure 1. XRD pattern of SAS.](image1)

![Figure 2. Contact angle of treated SAS powders.](image2)
The hydrophobicity of the SAS surface can be represented by the contact angle. Before Z6124 coating, the water droplets almost completely permeate into the SAS powders, it means that the unprocessed SAS powders have a contact angle of nearly 0°. However, the situation changed after the Z6124 was coated on the ceramic. The contact angle of modified SAS powders is shown in Figure 2. The contact angle is 146.2° indicating a hydrophobic nature. The result confirmed that SAS powders have been modified successfully. Figure 3 shows the infrared spectrum of the treated SAS. The peak at 3434 cm⁻¹ means that there is some -OH residue on the ceramic surface. The peaks at 1374 cm⁻¹ and 1453 cm⁻¹ indicate symmetric and asymmetric bending vibration of -CH₃, respectively. Moreover, the peak of stretching vibration of aromatic ring at 1630 cm⁻¹ testified again that SAS powders have been modified successfully.

3.2. Morphology of composites

Figure 4 shows the cross-sectional SEM images of SAS/PTFE composites. Obviously, the SAS powders mixed with PTFE well and the SAS powders distribution was uniform. It could be observed that the uniform component was formed through melted and recrystallized by hot pressing. Moreover, it testified the concluded that the hot pressing with 12 MPa at 370 °C for 2 h is sufficient to obtain the most density microstructure, which according the previous experiments.

3.3. Density and moisture absorption

Figure 5 shows the variation in density and the moisture absorption with volume fraction of SAS. As the amount of SAS increases from 10 vol. % to 50 vol. %, the density of the composite showed a continuous increase due to the high density of SAS (3.17g/cm³). Meanwhile, the increase in density decreases at higher SAS concentration range due to the increase in porosity with the SAS concentration. It is well known that moisture will degrade dielectric properties and is not conductive to the stability of composite. Meanwhile, the moisture absorption of composites is influenced by the surface of ceramics and the porosity of composites. As shown in Figure 5, the moisture absorption increases with SAS loading up to 50 vol. %. The interface area increases with SAS concentration is one of the reasons for this phenomenon, and the increased porosity of composites also augment the moisture absorption.
3.4. Dielectric constant ($\varepsilon_r$) and dielectric loss ($\tan\delta$)

In addition to the properties of the components, the dielectric properties of composites are also affected by other parameters, such as the dispersion of SAS, the porosity and the interfacial interaction between the SAS and PTFE. Figure 6 shows the variation in $\varepsilon_r$ and $\tan\delta$ with different volume fraction of SAS. Obviously, both $\varepsilon_r$ and $\tan\delta$ increased along with the increase of content of SAS. At the same time, the deviation between experimental dielectric constant and calculated dielectric constant
increases as the SAS increases due to increase in porosity[1]. As well know, \( \varepsilon_r \) of SAS is higher than PTFE, this is the main reason for the increase of \( \varepsilon_r \). Meanwhile, the quantity of polarized particles was increased with SAS concentration, which strengthened the dipole-dipole interaction lead to the increase of \( \varepsilon_r \) [22]. On the other hand, the similar variation trend was observed in dielectric loss of the composites. The proportion of interface area increases with SAS concentration increasing lead to anharmonicity and charge accumulation on the interface, which promoted the tan\( \delta \) of the composite. Even so, the composites display a low tan\( \delta \) (<0.002) even at 50 vol. % concentration.

![Image](image_url)  
**Figure 6.** The variation in \( \varepsilon_r \) and tan\( \delta \) with different volume fraction of SAS.

![Image](image_url)  
**Figure 7.** The variation in \( \tau_\varepsilon \) with different volume fraction of SAS.

### 3.5. Temperature coefficient of dielectric constant

The temperature coefficient of dielectric constant plays a significant role in applications for high-frequency packaging materials. A little variation of \( \tau_\varepsilon \) will cause the change in operating frequency of any devices with this materials. Figure 7 shows the variation of \( \tau_\varepsilon \) with respect to SAS concentration. It is obviously that the \( \tau_\varepsilon \) and \( \alpha_L \) of SAS are positive quantities, as shown in table 1, hence, the \( \frac{\partial \alpha}{\partial T} \) of SAS is also a positive quantity according to equation 2. The second term describes the change of polarized
particles due to the thermal expansion [1]. It is well known that the CTE of composites decreases with the increasing filler concentration, thus the decrease in $\alpha_c$ is one of the reasons for this phenomenon with increasing SAS concentration. Hence, the $\tau_c$ of PTFE was compensated by the SAS. Particularly, the $\tau_c$ of composite is 5.1 ppm/°C, when the volume of SAS is 40 vol. %.

4. Conclusion
In this study, the SAS was treated by Z6124 and filled into PTFE by SMECH process. FTIR testified that silane agent (Z6124) has modified SAS successfully. The density, the moisture absorption, the dielectric constant and the dielectric loss increased with the increase of SAS concentration. Meanwhile, the temperature coefficient of dielectric constant of composites was compensated by fillers and caused the change of $\tau_c$ from negative to positive value and it was obtained a value near zero. The authors were able to obtain a relatively low $\tau_c$ of 5.1 ppm/°C of SAS/PTFE with $\varepsilon_r$ of 3.21, tanδ of 0.00136 and moisture absorption of 0.03 % at 40 vol. % SAS concentration.

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