Surface-modified $\text{Zn}_{0.5}\text{Ti}_{0.5}\text{NbO}_4$ particles filled polytetrafluoroethylene composite with extremely low dielectric loss and stable temperature dependence

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Abstract: Polymer-ceramic composites are widely applied in microwave substrate materials due to the excellent dielectric properties and simple preparation process recently. Polytetrafluoroethylene-based (PTFE) composites filled with $\text{Zn}_{0.5}\text{Ti}_{0.5}\text{NbO}_4$ (ZTN) ceramic particles were fabricated by hot-pressing. The particles were modified by $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ to enhance the interface compatibility between PTFE and ZTN powders, which was characterized by X-ray photoelectron spectroscopy (XPS) and contact angle. The surface characteristic of particles transformed into hydrophobicity and tight microstructure as well as better dielectric properties were obtained after the surface modification. The microstructure, dielectric, thermal, mechanical properties, and water absorption of the composites concerning ZTN content were investigated. Modified ZTN/PTFE composites with 50 vol% ZTN particles exhibit excellent dielectric properties with a high dielectric constant of 8.3, an extremely low dielectric loss of 0.00055 at 7 GHz, and a stable temperature coefficient of the dielectric constant of $-12.2 \text{ ppm}/^\circ\text{C}$. All the properties show modified ZTN particles filled PTFE composite is the potential material for microwave substrate application.

Keywords: composites; dielectric properties; niobium; substrate

1 Introduction

Recently, the 5th-generation communication system, integrated circuit, satellite base station, auto anti-collision system, radar systems, and electronic navigation technology are developing rapidly, which puts forward the higher requirement for advanced substrate materials, peculiarly

guaranteeing the signal transmit with high speed and high frequency [1–3]. Because of the perfect combination properties and easy fabrication processing, ceramic particles filled polymer composite substrates have always been paid close attention. In all kinds of polymer, PTFE exhibits huge advantages for advanced substrate materials due to the low dielectric constant (ϵ), low dielectric loss ($\tan\delta$), and perfect chemical and thermal stability. However, the high coefficient of thermal expansion (CTE) and poor temperature coefficient of dielectric constant (τ_ϵ) limit application for substrate

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material. Therefore, various particles had been filled in PTFE to fabricate composites for microwave substrate application [4,5].

PTFE-based substrate material with high ϵ has attracted increasing attention due to the specific application in recent years. In previous studies, PTFE/ $0.55\text{ZrTi}_2\text{O}_6$ – $0.45\text{ZnNb}_2\text{O}_6$ composites exhibited the best dielectric properties: $\epsilon = 7.32$, $\tan\delta = 0.0015$, and $\tau_e = -84$ ppm/°C (10 GHz) at the powder content of 46 vol% [6]. The $(\text{Na}_{0.6}\text{Li}_{0.4})_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ and glass fiber were filled into PTFE matrix to fabricate composite substrate, and the composites showed the best dielectric properties: $\epsilon = 10.4$, $\tan\delta = 0.0026$ (10 GHz), and excellent $\tau_e = -0.9$ ppm/°C when the weight fraction of fillers was 60 wt% [7]. PTFE/ $\text{Ca}_{0.55}\text{Nd}_{0.3}\text{TiO}_3$ (CNT) composites possessed the best dielectric properties: $\epsilon = 12$, and low $\tan\delta = 0.00085$ (10 GHz) at 50 vol% filler contents; the PTFE/ $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ composite exhibited the dielectric properties: $\epsilon = 6.7$, $\tan\delta = 0.003$ (X-band) when the weight fraction of particles was 76 wt%, but the τ_e of both composites were not studied [8,9]. The ϵ , $\tan\delta$, and τ_e have always been the key properties for substrate materials. The ϵ determines the application fields of substrates, $\tan\delta$ influences the signal transmission loss, and the τ_e affects the temperature dependence of dielectric property and the application outdoors. The ϵ , $\tan\delta$, and τ_e can be adjusted by changing the volume fraction of fillers. However, according to the previous studies, the fabrication of substrate materials with high ϵ , extremely low $\tan\delta$ (< 0.001), and stable τ_e simultaneously, is still very tough, which primarily ascribes the hardness of manufacture of appropriate particles with advanced dielectric properties.

As reported in Ref. [10], $\text{Zn}_{0.5}\text{Ti}_{0.5}\text{NbO}_4$ (ZTN) microwave dielectric ceramic exhibited dielectric properties with high ϵ of 37.4, ultrahigh $Q \times f$ of 194,000 GHz and negative temperature coefficient of resonant frequency (τ_f) of -58 ppm/°C, which is theoretically the potential fillers for the exploitation of substrate materials with high ϵ , low $\tan\delta$, and can compensate the poor τ_e of PTFE to obtain composites with appropriate τ_e . Meanwhile, PTFE and ZTN ceramic particles own different surface properties, which would cause the usual problem (antipathic interface) in polymer-ceramic composites [11]. The surface modification of ceramic powders through coupling agents is an effective approach to solve the problem. KH550, PTMS, TEOS, TBT, and $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$, etc. have been applied in various polymer-ceramic systems according to the

component of the polymer matrix [12–15]. Recently, $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ has been used in PTFE-based composites due to the special function groups of $-\text{OCH}_2\text{CH}_3$ which can be hydrolyzed and $-(\text{CF}_2)_5\text{CF}_3$ similar to the structure of PTFE matrix [3]. Because of the two functional groups, $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ can act as the “bridge” between the PTFE matrix and ZTN powders, which could enhance the interface compatibility and improve consistency. In this study, ZTN ceramic particles were treated using $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$, and then filled in PTFE to fabricate ZTN/PTFE composites. The effects of ZTN loading on morphology, dielectric, thermal, mechanical properties, as well as moisture absorption and the microstructure, dielectric properties of untreated ZTN/PTFE composites, had been investigated systematically.

2 Experimental

2.1 Fabrication of ZTN ceramic powders

ZTN ceramic powders were synthesized according to the solid-state method. ZnO , TiO_2 , and Nb_2O_5 powders (all with 99.99% purity) were purchased from Aladdin Biochemical Technology Co., Ltd., China, and weighed following the ZTN stoichiometric ratio. All the powders were mixed with ethyl alcohol and underwent a ball-milling process for 12 h. After drying at 80 °C for 24 h removing ethanol, the mixture was calcined for 4 h at 1100 °C. The powders went through the ball-milling process again for 24 h and dried at 80 °C to acquire homogeneous particle size.

2.2 Surface modification of ZTN ceramic powders

As shown in Fig. S1 in the Electronic Supplementary Material (ESM), the content of $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ (TCI Corporation, Japan) should be fixed at 2 wt% of ZTN powders. $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ and deionized water were added into ethanol and mixed at 55 °C for 1 h. Afterwards, all the solution was mixed with the suspension of ZTN powders and ethanol at 60 °C for 6 h. The surface-treated ZTN powders were acquired after the heat treatment for 24 h at 120 °C.

2.3 Fabrication of ZTN/PTFE composites

The volume fractions of ZTN particles in the composites changed from 20 vol% to 60 vol%. PTFE suspension and ZTN powders were weighed and mixed using magnetic-stirring for 12 h. Afterwards, the above

mixture was heated to 100 °C for 24 h to wipe off the absorbed water and ethanol, and then dried at 280 °C for 6 h to remove the surfactant in suspension. ZTN/PTFE composites were synthesized through hot-pressing sintering at 25 MPa and 360 °C for 2 h. The diagram illustrating the fabrication of modified ZTN/PTFE composites is shown in Fig. 1.

2.4 Characterization

The morphology of untreated ZTN powders, modified ZTN powders, surface, and cross-sectional images of ZTN/PTFE composites were characterized by the field emission scanning electron microscopy (FESEM; SU8010, Hitachi Ltd., Japan). Untreated and modified ZTN powders were added into ethanol and the uniform suspension was obtained by ultrasonic treatment for 30 min. Then, the suspension was poured onto the surface of alumina tape and dried to fabricate samples for SEM. The composites were put in liquid nitrogen and fractured to obtain the SEM samples for cross-sectional images. The porosity and density of all samples were measured by Archimedes' method. The surface modification of ZTN powders was characterized by X-ray photoelectron (XPS; Al K α , AXIS SUPRA, UK) and Fourier transform infrared spectrometer (FTIR, Nicolet 5700, Thermo Nicolet, USA). X-ray powder diffraction (XRD, EMPYREAN, PANalytical Co., the Netherlands) with Cu K α radiation was employed to

characterize the crystal phase of ZTN powders and ZTN/PTFE composites. The video-based contact angle measuring device (OCA 20, Dataphysics, Germany) was used to reveal the variation of the contact angle on the surface of ZTN powders. The laser particle analyzer (Beckman Coulter LS13320, USA) was employed to study the particle size distribution of ZTN powders. The dielectric properties were measured by Agilent E5071C network analyzer according to the Hakki and Coleman method in the TE₀₁₁ mode at about 7 GHz. The flexure strength was tested by the universal materials testing machine (CMT5205) according to IPC-TM-650 2.4.4B. TMA SS7300 was utilized to measure the coefficient of thermal expansion (CTE) according to IPC-TM-650 2.4.41. The moisture absorption was studied on the basis of IPC-TM-650 2.6.2. Hot Disk TPS 2500S was employed to measure the thermal conductivity and thermal diffusivity with the isotropic model.

3 Results and discussion

3.1 Microstructure analysis

The XRD pattern of ZTN ceramic powders and ZTN/PTFE composite is exhibited in Fig. 2. Peaks of ZTN powders are consistent with the result of Tseng's work [10], which indicates that Zn_{0.5}Ti_{0.5}NbO₄ is

Fig. 1 Schematic illustration of the fabrication of modified ZTN/PTFE composites.

Fig. 2 XRD patterns of ZTN powders and ZTN/PTFE composites.

fabricated successfully and there are no impurity phases. XRD patterns of ZTN/PTFE composites are composed of the peaks of the PTFE matrix and ZTN ceramic. The peak at about 18° matches with PTFE (#JCPDS 00-054-1595) and PTFE peak height decreases persistently with the ZTN loading increases, which is attributed to the relation between the peak height and the content of components. Furthermore, there are no other phases that existed in the composites, which manifest that the uniform mixture is fabricated and the ZTN ceramic powders as well as PTFE show perfect chemical stability.

XPS, FTIR, and contact angle change are utilized to characterize surface modification of ZTN particles. The elements in both modified and untreated particles were detected by XPS full spectrum and the carbon fine spectrum was used to reveal carbon states in different organic groups that existed in $C_{14}H_{19}F_{13}O_3Si$. Due to the hydrophobicity caused by $C_{14}H_{19}F_{13}O_3Si$ modification, the change of contact angle of untreated and modified ZTN powders was characterized. Figure 3 shows the XPS full spectra of untreated and modified ZTN particles. Zinc, oxygen, titanium, carbon, and niobium can be detected in both the spectra and every corresponding peak in the two spectra shows nearly the same position [16], which is attributed to the elemental composition of $Zn_{0.5}Ti_{0.5}NbO_4$. However, the obvious F_{1s} and F_{Auger} peaks appear in the modified ZTN powders, and in the same energy position, no peak exists in untreated ZTN particles, which ascribes F in $C_{14}H_{19}F_{13}O_3Si$ coated on the surface of modified ZTN powders. Meanwhile, there is only one obvious and strong carbon peak in the untreated powders, but in the modified ZTN powders, different carbon peaks appear,

which confirms that there are different carbon states with various binding energy. The fine carbon spectrum was used to characterize the carbon states of modified powders. The spectra of raw data, fitting peak sum, and C-H, C-F₂, C 1s, C-F, C-F₃ with a binding energy of 283.6, 290.5, 284.8, 289.8, and 292.9 eV respectively are exhibited in Fig. 4. It is evident that fitting peak sum spectrum matches with raw data basically, which confirms that $(CH_2)_2-(CF_2)_5-CF_3$ existed in $C_{14}H_{19}F_{13}O_3Si$ would cause the appearance of different carbon states and the deviation of carbon binding energy. The untreated powders only show the C 1s peak, indicating that $C_{14}H_{19}F_{13}O_3Si$ has been introduced into the modified ZTN powders. To highlight the huge improvement in the hydrophobic property of particles through modification of $C_{14}H_{19}F_{13}O_3Si$, the contact angle of untreated as well as modified particles is shown in Fig. 5. The untreated ZTN powders exhibit hygroscopicity with the contact angle of 16.6° , and after the modification, the contact angle is improved to 139° , which indicates

Fig. 3 XPS spectra of modified ZTN powders and untreated ZTN powders.

Fig. 4 Carbon XPS spectra of modified ZTN powders.

Fig. 5 Contact angles of water drop on (a) the modified ZTN powders and (b) untreated ZTN powders.

the strong hydrophobicity of modified ZTN powders caused by long $-\text{CF}_2-$ chain. Meanwhile, the FTIR spectrum was also used to show the surface modification of ZTN powders and explained whether $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ still exists on the surface of powders after the high-temperature treatment during the fabrication of composites. Figure S2 in the ESM shows the FTIR spectra of original, modified powders, and modified powders through 380°C heat treatment. All the spectra own the peak at 3435 cm^{-1} , which is corresponding to the $-\text{OH}$ on the surface of powders. Many complex peaks in the range of $1000\text{--}1500\text{ cm}^{-1}$ appear in the spectra of modified powders and modified powders through heat treatment, which may be the $\text{C}-\text{F}_2$ and $\text{C}-\text{F}_3$ groups because the infrared characteristic peaks of these groups are easily affected by other organic groups and specific peak positions can not be confirmed. However, in the same wavenumber range, no peaks

appear in the FTIR spectrum of original ZTN powders, which demonstrates that the surface of ZTN powders has been modified successfully by $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ and the high-temperature heat treatment during the fabrication of composites would not destroy the modification effect drastically. All the results concluding XPS, FTIR, and contact angle can confirm that $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ has covered ZTN powders successfully. Due to special groups of $-(\text{CF}_2)_5-\text{CF}_3$ existed in $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$, particularly $-\text{CF}_2-$ similar to the structure of PTFE matrix, the interface compatibility between ZTN ceramic and PTFE can be forecasted to be improved by the modification of silane coupling agent, which would influence the microstructure and properties of composites theoretically.

The property of particles filled polymer composite chiefly depends on the property of every component. Nevertheless, particle size, morphology features, uniformity, and interface compatibility between ceramic and polymer are also significant [17,18]. Figure 6 shows the SEM images of original, modified ZTN powders, and the particle size distribution of ZTN powders. It is evident that untreated particles are severely agglomerated and the surface is rough, which could impute that the raw ZTN powders own strong hygroscopicity and too many $-\text{OH}$ groups on the surface cause strong interaction between the powders. The modified powders are well-dispersed and show a smooth surface, which is due to that the modification of $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ can form the coated polymer layer on the surface of the powder to decrease the binding force between the powders. The particle size distribution of ZTN particles has been characterized and exhibited in Fig. 6(c). The particle size is distributed uniformly in the range of $0\text{--}4\text{ }\mu\text{m}$ and the mean size is about $1.3\text{ }\mu\text{m}$.

Figure 7 shows the surface morphology features of modified ZTN powders filled PTFE composites with the ceramic loading from 20 vol% to 60 vol% and the untreated ZTN/PTFE composites with ZTN loading of

Fig. 6 SEM images of (a) untreated ZTN powders and (b) modified ZTN powders; (c) particle size distribution of modified ZTN powders.

40 vol%. All the composites with the volume fraction of ZTN powders below 60 vol% exhibit smooth and compact surface, whereas many pores appear on the surface when the loading of powders reaches 60 vol%, which is due to that the PTFE matrix could encase the particles absolutely at relative low ZTN loading and the particles will contact with each other when the content of powders exceeds polymer matrix. Hence, there would be pores, defects, and powders that appeared on the composite's surface. Untreated ZTN/PTFE composites with the loading of the ceramic powder of 40 vol% are also depicted in Fig. 7(f) to compare with the modified ZTN powders filled PTFE composites to show the influence of $C_{14}H_{19}F_{13}O_3Si$ on the surface morphology.

The surface of untreated ZTN/PTFE composite is rougher than the modified one and many pores appear, which is attributed to the improvement of dispersity and the interface compatibility between powders and the polymer caused by the modification. The cross-sectional micrographs of modified ZTN/PTFE composites with powder contents within 20–60 vol% and untreated ZTN powders filled PTFE composite with 60 vol% ceramic loading are exhibited in Fig. 8. When the volume fraction of ZTN powders stay between 20 vol% and 50 vol%, all the cross-sectional images of modified ZTN/PTFE composites exhibit relatively compact microstructure, and increasing pore amount and particles do not aggregate in the polymer matrix, which is owing

Fig. 7 Surface SEM micrographs of modified ZTN/PTFE composites: (a) 20 vol%, (b) 30 vol%, (c) 40 vol%, (d) 50 vol%, (e) 60 vol%, and (f) untreated ZTN/PTFE composite of 40 vol%.

Fig. 8 Cross-sectional SEM micrographs of modified ZTN/PTFE composites: (a) 20 vol%, (b) 30 vol%, (c) 40 vol%, (d) 50 vol%, (e) 60 vol%, and (f) untreated ZTN/PTFE composite of 60 vol%.

to that the powders can be wrapped by PTFE completely at such low powder loading. Nevertheless, when the ZTN loading reaches 60 vol%, many pores and the agglomeration appear in the cross-section, which ascribes the less volume fraction of polymer than ZTN powders. Meanwhile, the cross-sectional image of untreated ZTN/PTFE composites with ceramic powder loading of 60 vol% is shown in Fig. 8(f). Compared to the modified ZTN/PTFE composites with the same loading, the untreated ZTN/PTFE composites exhibit more pores and detects as well as loose microstructure, which confirms that the interface compatibility between ZTN powders and PTFE matrix is feeble in untreated ZTN/PTFE composites. The feeble compatibility is on the account of the enormous discrepancy existed in the interface energy of untreated powders and PTFE due to the extremely low surface energy of the PTFE matrix. Modification of $C_{14}H_{19}F_{13}O_3Si$ improves the dispersibility of ZTN powders and the interface compatibility between particles and PTFE as shown in Figs. 6–8. Finally, compact and uniform microstructure for ZTN/PTFE composite is acquired, which ensures excellent properties.

Figure 9 depicts the element mapping and content of all elements in cross-section of modified ZTN/PTFE composite with ZTN loading of 50 vol%. All the elements are detected to be the same with the components of ZTN ceramic and PTFE, such as zinc, titanium, oxygen, niobium, carbon, and fluorine. Meanwhile, all the elements are well-dispersed which manifest the homogeneous microstructure has been formed. The content of all elements investigated by SEM–EDS shown in Fig. 9(g) is corresponding to the ratio of ZTN powders and PTFE matrix, which verifies the reliability of experimental data.

3.2 Density, porosity, and water absorption

The porosity and relative density are the significant properties for substrate materials, which is due to that the moisture absorption, dielectric, and mechanical properties are influenced by the porosity. Table 1 shows the bulk density, theoretical density, porosity, relative density, and moisture absorption of different composites. The densities of ZTN ceramic and PTFE polymer are 5.14 and 2.2 g/cm³, respectively. With the volume

Fig. 9 Corresponding element mappings of (a–f) Zn, Ti, O, Nb, C, and F, respectively; (g) EDS spectra and element content of ZTN/PTFE composite with 50 vol% loading.

Table 1 Bulk density, theoretical density, porosity, relative density, and moisture absorption of modified ZTN/PTFE composites

Volume fraction of ZTN (vol%)	Bulk density (g/cm ³)	Theoretical density (g/cm ³)	Porosity (%)	Relative density (%)	Moisture absorption (wt%)
20	2.774	2.788	0.47	99.53	0.021
30	3.061	3.082	0.68	99.32	0.024
40	3.322	3.376	1.58	98.42	0.07
50	3.541	3.67	3.51	96.49	0.13
60	3.742	3.964	5.6	94.4	0.95

fraction of ZTN powders increasing, porosity and moisture absorption all exhibit the increase, whereas relative density decreases. The porosity of ceramic particles filled polymer composites mainly depends on the contact among the particles and the interface compatibility between the polymer and fillers. The probability of contact among particles would increase as ZTN particle loading increases, thus resulting in an increase of porosity as well as the decrease of relative density. Moisture absorption is influenced by the porosity and relatively high porosity would cause higher moisture absorption. However, the porosity as well as water absorption maintains low levels when ZTN volume fraction is below 60 vol%, which can ascribe that particles can be encased absolutely by polymer to form tight microstructure at a low loading of fillers. As ZTN particle content reaches 60 vol%, the porosity and water absorption become higher, which is mainly due to the relatively less proportion of PTFE and too much contact among the particles. Meanwhile, all the above results can be confirmed from the microstructure of all the composites shown in Fig. 8. Generally, the following equations are used to calculate the theoretical density (ρ_0) and the water absorption (W):

$$\rho_0 = \sum_a \rho_a V_a \quad (1)$$

$$V_a = \frac{\frac{m_a}{\rho_a}}{\sum_a \frac{m_a}{\rho_a}} \quad (2)$$

$$W = \frac{m - m_0}{m_0} \quad (3)$$

$$\rho_r = \frac{\rho}{\rho_0} \quad (4)$$

$$p = \left(1 - \frac{\rho}{\rho_0}\right) \times 100\% \quad (5)$$

where ρ_a , V_a , m_a represent density, volume proportion, and the weight of filled particles and polymer, respectively. m and m_0 represent the weight of substrate materials after absorbing moisture and primary weight, respectively. ρ_r and p represent the relative density and the porosity of composite, respectively. ρ and ρ_0 are the experimental density and theoretical density, respectively.

3.3 Dielectric properties

The ε , $\tan\delta$, and τ_e are the pivotal properties for substrate materials applied in the microwave frequency band. Many factors are influencing the dielectric properties of substrate materials, especially the properties of the individual component. However, the pores and defects in the substrate materials are other significant elements. As depicted in Figs. 10(a) and 10(b), the ε and $\tan\delta$ of untreated and modified ZTN/PTFE composites are characterized. As the volume proportion of ZTN particles increases from 20 vol% to 60 vol%, the ε and $\tan\delta$ of both kinds of ZTN/PTFE composites all exhibit the increase. The ε in the microwave frequency band mainly depends on the electron displacement polarization and ionic displacement polarization of materials. In the usual microwave frequency band, ε is mainly related to the microstructure of the material and is not influenced obviously by the frequency. Hence, the dielectric constant of composites mainly depends on the dielectric constant of every component and ZTN ceramic possesses ε of 37.5 which is much higher than the ε of PTFE (Section 2.2). Hence, the growth of ε of ZTN/PTFE composites is attributed to the growing volume fraction of ZTN ceramic particles with higher ε . The $\tan\delta$ of the PTFE matrix and ZTN ceramic particles are the main factors influencing the $\tan\delta$ of ZTN/PTFE composites. PTFE owns the dielectric loss of about 0.0001 at high frequencies and ZTN ceramic possesses extremely low dielectric loss of about 0.0002 at around 7 GHz, thus making the $\tan\delta$ of all composites with various

ZTN contents stay in low values (< 0.001) and even the $\tan\delta$ of modified ZTN/PTFE composites with the particle loading of 60 vol% is just 0.0009. Nevertheless, the pores are increasing continually with the growth of ZTN loading, which could be confirmed by the results of porosity analysis and SEM images. As for substrate materials, pores are another significant factor affecting the $\tan\delta$, which can explain why $\tan\delta$ is increasing persistently with the ZTN loading increasing [19]. When the volume fraction of ZTN stays between 20 vol% and 50 vol%, the porosity of all the composites maintains a low value, which would cause the minor fluctuation of $\tan\delta$. Meanwhile, it is worth noting that the untreated ZTN/PTFE composites own inferior dielectric properties with lower ε and higher $\tan\delta$ compared with improved ZTN/PTFE composites, which is mainly attributed to porosity discrepancy through modification of $C_{14}H_{19}F_{13}O_3Si$. From an analysis of cross-sectional SEM micrographs of untreated and modified ZTN/PTFE composites, modified ZTN filled PTFE composites exhibit tighter microstructure and fewer pores. High porosity would cause the reduction of ε and growth of $\tan\delta$.

Meanwhile, to confirm that the experimental data of ε is credible and predictable, the famous model (effective medium theory (EMT)) for the theoretical ε of polymer-based composites filled with ceramic powders was listed and compared with experimental ε . The equation for EMT model is shown as follows [20]:

$$\varepsilon_{eff} = \varepsilon_m \left[1 + \frac{V_f(\varepsilon_f - \varepsilon_m)}{\varepsilon_m + m(1 - V_f)(\varepsilon_f - \varepsilon_m)} \right] \quad (4)$$

where ε_{eff} , ε_m , and ε_f represent the theoretical dielectric constant, dielectric constant of polymers as well as ceramic, respectively. V_f is the volume fraction of ceramic particles. The value of m is 0.25, which depends on the morphology and microstructure of the composites. Figure 10(c) shows the EMT model matches the experimental dielectric constant well and the same conclusion was also obtained in Ref. [8].

Due to that the τ_ε of PTFE matrix is about -400 ppm/ $^{\circ}C$, the application of PTFE-based substrates is limited immensely out of doors. The calculation equation for τ_ε of ceramic filled composites is as follows:

$$\tau_\varepsilon = \frac{\varepsilon}{3} \left(\frac{1}{\alpha} \frac{\partial \alpha}{\partial T} - 3\alpha_L \right) \quad (5)$$

where ε is the dielectric constant of the composites,

$\frac{1}{\alpha} \frac{\partial \alpha}{\partial T}$ represents the variation in the polarization of composites, and α_L is the coefficient of thermal expansion. As for ZTN filled PTFE composites, $\frac{1}{\alpha} \frac{\partial \alpha}{\partial T}$ and α_L exhibit positive values. The addition of ZTN ceramic particles can improve the polarization of composites due to the higher polarization ability of ZTN (higher dielectric constant) compared with the PTFE matrix and decrease α_L simultaneously, which would cause the improvement of the value of $\left(\frac{1}{\alpha} \frac{\partial \alpha}{\partial T} - 3\alpha_L \right)$

with the increase of ZTN volume fraction. Furthermore, as shown in Fig. 10, the ε of the composites also increases with increasing of ZTN loading. All the above variations can cause the improvement of the τ_ε of the composites according to Eq. (5). Ref. [9] showed better properties were often acquired at high filler loadings, especially the appropriate τ_ε and low CTE. Therefore, the modified ZTN/PTFE composites with 20 vol% and 30 vol% filler loading are not studied. It is shown in Fig. 10(d) that the τ_ε (temperature range of 25 – 80 $^{\circ}C$) increases from -98.9 to 24.4 ppm/ $^{\circ}C$ when the volume fraction increases from 40 vol% to 60 vol%. The τ_ε of ZTN/PTFE composites are regulated to -12.2 ppm/ $^{\circ}C$ at the volume fraction of 50 vol%, which is stable for the substrate materials with high ε and shows huge preponderance compared with the previous studies.

3.4 Thermal properties

Figure 11 exhibits the thermal conductivity and thermal diffusivity of modified ZTN/PTFE composites containing various ceramic particles loading. When the volume fraction of ZTN varies from 20 vol% to 50 vol%, the thermal conductivity changes from 0.37 to 0.52 W/(m·K) and the thermal diffusivity shows the same increase with the variation from 0.13 to 0.25 mm²/s, which ascribes high thermal conductivity, high thermal diffusivity of ZTN ceramic powders compared with PTFE matrix, and the construction of thermal conductive path by ZTN particles. Nevertheless, the ZTN/PTFE composites with 60 vol% ceramic particles own inferior thermal conductivity and thermal diffusivity than 50 vol%, which may ascribe the higher porosity of ZTN/PTFE composites with 60 vol% powders. The pores possess very poor thermal conductivity and cause the separation between polymer and fillers, which may block heat transfer in the composites and result in low thermal

Fig. 10 (a) Dielectric constant and (b) dielectric loss of untreated and modified ZTN/PTFE composites, (c) comparison of experimental and theoretical dielectric constant, and (d) the temperature stability of dielectric constant.

Fig. 11 Thermal conductivity and thermal diffusivity of ZTN/PTFE composites.

conductivity as well as low thermal diffusivity of the composites. Therefore, the best thermal conductivity and thermal diffusivity were obtained at the ZTN volume fraction of 50 vol% with 0.52 and 0.25 mm²/s, respectively.

The printed circuit board (PCB) is fabricated by adhering copper foil with substrate materials and for the sake of preventing delamination between copper foil and substrates during the drilling process, the *CTE* of substrates should match with copper foil. However,

the PTFE matrix possesses a high *CTE* of about 109 ppm/°C, which is much larger than the copper foil (18 ppm/°C). The best way to adjust the *CTE* of substrates near to copper foil is filling modification. Figure 12 depicts the dynamic mechanical curves and *CTE* of ZTN/PTFE composites change within 96–25 ppm/°C when the volume fraction of ZTN varies from 20 vol% to 60 vol%, which is mainly on account of the extremely low *CTE* of ZTN ceramic particles compared with PTFE. At last, at the ZTN volume fraction of 50 vol%, the substrate materials with acceptable *CTE* of 34 ppm/°C are fabricated, which prevents the delamination to some extent.

3.5 Mechanical properties

The load-deflection curve, flexure strength of modified ZTN/PTFE composites including different ZTN loadings are shown in Fig. 13. The maximum force shown in Fig. 13(a) and the flexure strength shown in Fig. 13(b) all increase when the volume fraction changes from 20 vol% to 40 vol%. When the volume proportion of ZTN reaches 50 vol% and 60 vol%, the flexure strength decreases compared with the composites with 40 vol% ZTN powders. The polymer crosslink density, pore,

Fig. 12 (a) Dynamic mechanical curves and (b) CTE of ZTN/PTFE composites.

Fig. 13 (a) Variation of the load-deflection curve and (b) the flexure strength of ZTN/PTFE composites.

Table 2 Comparison of comprehensive properties of this study with other high dielectric constant PTFE-based composites

Filler	Loading	ϵ	$\tan\delta$	F (GHz)	τ_c (ppm/°C)	CTE (ppm/°C)	Moisture absorption (%)	Ref.
TeO ₂	60 vol%	5.6	0.006	7	—	32	—	[23]
Ba (Mg _{1/3} Nb _{2/3}) O ₃	68 wt%	5.84	0.0015	10	—	—	—	[2]
(Ca,Li,Sm)TiO ₃	50 wt%	6.22	0.0012	10	—	—	—	[15]
Ba (Mg _{1/3} Ta _{2/3}) O ₃	76 wt%	6.7	0.003	X-band	—	—	0.072	[9]
0.55ZrTi ₂ O ₆ –0.45ZnNb ₂ O ₆	46 vol%	7.32	0.0015	10	–84	17.5	—	[6]
ZrTi ₂ O ₆	46 vol%	7.42	0.0022	10	–89	20	0.15	[24]
Li ₂ Mg ₃ TiO ₆	70 wt%	6.17	0.0019	10	123	—	0.16	[25]
(Na _{0.6} Li _{0.4}) _{0.5} Nd _{0.5} TiO ₃ +glass fiber	60 wt%	10.4	0.0026	10	–0.9	—	0.34	[7]
Ba _{4.2} Nd _{0.2} Ti ₁₈ O ₅₄	70 wt%	10.6	0.004	11.5	—	18	—	[26]
Ca _{0.5} Nd _{0.3} TiO ₃	50 vol%	12	0.00085	10	—	35	0.27	[8]
CaTiO ₃	40 vol%	13	0.0053	5	—	—	—	[27]
Zn _{0.5} Ti _{0.5} NbO ₄	50 vol%	8.3	0.00055	7	–12.2	34	0.13	This study

and defect would influence mechanical properties of composites [21]. When ZTN content ranges between 20 vol% and 40 vol%, all the composites own high specific density and low porosity. Hence, PTFE crosslink density is the main influence factor. The ZTN powders

play a certain role as the nucleating agent for the PTFE matrix, which may improve the crosslink density and make the polymer matrix become uniform [21,22]. So, the flexure strength and maximum force are improved by ZTN powders at low filler loadings. However, when

the volume fraction increases to 50 vol% and 60 vol%, the high porosity and more defects cannot be ignored and become the primary affecting factors. The pores and defects would weaken the interaction force between the polymer and ZTN powders, which causes a decrease of flexure strength and the maximum force. Eventually, the appropriate flexure strength of 23 MPa for ZTN/PTFE composites is obtained when the loading of fillers is 50 vol%.

To highlight the dedication of modified ZTN/PTFE composites for substrate materials, Table 2 exhibits the previous studies concerning high ϵ PTFE-based substrate materials [23–27]. ZTN/PTFE composites with high ϵ (8.3), extremely low $\tan\delta$ (0.00055), and highly stable τ_e (-12.2 ppm/ $^{\circ}\text{C}$) show excellent dielectric properties in high ϵ PTFE-based substrate materials. Simultaneously, the thermal conductivity, CTE , moisture absorption, and flexure strength are all appropriate for the substrate materials. Therefore, the $\text{Zn}_{0.5}\text{Ti}_{0.5}\text{NbO}_4$ ceramic particles are the perfect filler for PTFE-based substrate materials [28–35].

4 Conclusions

PTFE-based substrate materials filled with $\text{Zn}_{0.5}\text{Ti}_{0.5}\text{NbO}_4$ (ZTN) particles modified by $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ were fabricated by hot-pressing. The results of XPS and contact angle showed the surface of particles had been modified successfully. Tight microstructure and superior dielectric properties were also obtained after the modification. The dielectric, thermal, mechanical, morphology, porosity, and water absorption of ZTN/PTFE composites were studied systematically. As ZTN ceramic particles content increases within 20–60 vol%, ϵ and $\tan\delta$ both exhibit the growth, whereas $\tan\delta$ stays low value at various ZTN contents, which is on account of the extremely low $\tan\delta$ of PTFE matrix and ZTN ceramic. The τ_e of PTFE was compensated by ZTN ceramic from about -400 to -12.2 ppm/ $^{\circ}\text{C}$. The ZTN/PTFE composite possesses excellent dielectric properties at 50 vol% filler content: high ϵ of 8.3, extremely low $\tan\delta$ of 0.00055 at 7 GHz, and stable τ_e of -12.2 ppm/ $^{\circ}\text{C}$ as well as other appropriate properties including water absorption of 0.13%, CTE of 34 ppm/ $^{\circ}\text{C}$, the thermal conductivity of 0.52 W/(m·K), and flexure strength of 23 MPa. Therefore, $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}$ modified ZTN ceramic particles filled PTFE composite is latent material for microwave substrates.

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Electronic Supplementary Material

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