Journal of Alloys and Compounds 803 (2019) 145-152

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Newly developed polytetrafluoroethylene composites based on F8261-modified Li₂Mg_{2.88}Ca_{0.12}TiO₆ powder



ALLOYS AND COMPOUNDS

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ARTICLE INFO

Article history: Received 18 February 2019 Received in revised form 1 June 2019 Accepted 9 June 2019 Available online 11 June 2019

Keywords: PTFE LMCT Surface characterization Dielectric properties

ABSTRACT

Li₂Mg_{2.88}Ca_{0.12}TiO₆ (LMCT) was modified by silane coupling agent (C₁₄H₁₉F₁₃O₃Si, F8261), and then filled in polytetrafluoroethylene suspension (PTFE) using hot treating approach. The weight fraction of LMCT varied from 30 to 70 wt %. XRD patterns presented the crystal phase of LMCT powders. The analyses of TEM, XPS, and FTIR were performed to characterize the surface states of LMCT fillers. The effects of LMCT filling content on the microstructure and dielectric properties were also investigated. Several theoretical models were discussed and compared with the dielectric constant of LMCT/PTFE substrates with respect to different LMCT content. Furthermore, the temperature and frequency dependence of dielectric constant were also considered on the composites. At last, the LMCT/PTFE composite substrates possessed relatively high dielectric constant (e_r = 4.33) and extremely low dielectric loss (tan δ = 0.001) at filler loading of 50 wt % LMCT.

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1. Introduction

Currently, the development and evolution of high integrated microwave circuit devices are becoming gradually confined by printed wiring board (PWB) substrates which are mainly comprised of organic polymer and inorganic fillers. The PWB substrates, especially the polymer based and ceramic filled substrates, have played a vital role in circuit design, which requires high working frequency, good temperature stability, easy processing and excellent dielectric properties [1]. To achieve substrate materials with a wide range of properties, various kinds of polymers and ceramic fillers with different dielectric property have been explored [2–7]. Among these polymers, polytetrafluoroethylene (PTFE) is a thermoplastic polymer with excellent electric properties of low dielectric loss (tan δ ~0.0003) and stable dielectric constant (ε_r ~2.1)

over a wide range of frequencies [8]. However, the main disadvantage of PTFE is the negative temperature coefficient of dielectric constant (τ_{ϵ} ~-400 ppm/°C) making it difficult to be used in microwave circuit devices. Generally, ceramic fillers have suitable dielectric constant, low loss tangent and relatively high thermal conductivity [9–11]. According to our previous reports [12–15], Li₂Mg_{2.88}Ca_{0.12}TiO₆ (LMCT) is a promising microwave ceramic with suitable dielectric constant ($\varepsilon_r = 17.9$), splendid quality factor $(Q \times f = 100000 \text{ GHz})$, and extremely low dielectric loss (tan δ = 0.0001). It is likely that LMCT filled PTFE composites will also exhibit excellent dielectric properties in the application of microwave devices. During the past decade, there were many studies on tailoring the dielectric, mechanical and thermal properties of polymers based and ceramics filled composites [16-18]. There is a strong demand to acquire an optimal composite which could simultaneously fulfill diverse applications.

However, due to the incompatible surface microstructure, it is difficult for organic polymer to cover the surface of inorganic fillers without any defects. Bad adhesion between polymer matrix and fillers adversely affects the comprehensive properties of the composites. Traditional PWB substrates have limited dielectric and mechanical properties in the most of microwave devices, which is mainly due to the difference surface structure existed between

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organic polymer and inorganic filler [19]. The influences of various coupling agents have been studied to improve the interface of ceramic filled polymer composites [19–23]. The coupling agent changes the surface characterizations of inorganic fillers by grafting molecular chain on the surface of filler particles. Hence, coupling agent acts as a "bridge" between inorganic fillers and organic polymers. Many studies have been conducted to research the influences of coupling agents on the composites. Majority of these studies focused on the final performances of the composites. However, to date, few investigations have been carried out to discuss the surface states and characterizations of the coupling agent modified fillers.

In present work, LMCT particles were used as fillers to adjust the properties of PTFE based composite substrates. LMCT powders were fabricated using typical solid state ceramic approach. The weight fraction of LMCT changed from 30 wt % to 70 wt %. $C_{14}H_{19}F_{13}O_3Si$ (F8261) was utilized as coupling agent to optimize the surface of LMCT filler. The surface characterization of untreated LMCT and modified LMCT was investigated in detail in this paper. The dielectric properties and microstructure of the composite substrates were also discussed at length.

2. Experiment

2.1. Fabrication of Li₂Mg_{2.88}Ca_{0.12}TiO₆ powders

To fabricate Li₂Mg_{2.88}Ca_{0.12}TiO₆ particles, reagent grade powders with at least 90% purity of CaCO₃ (MgCO₃)₄Mg(OH)₂·5H₂O, TiO₂ and Li₂CO₃ were selected as raw materials. All kinds of raw materials were weighed on the basis of stoichiometric ratio. Then mixed and grinded in alcohol solution for 5 h with ball milling. The obtained mixtures were baked and calcined at 1275 °C for 6 h. Later, the calcined powders were reground for 2 h to acquire LMCT powders with particle size of 15 µm. After the milling process, the suspensions were baked at 70 °C for 12 h. Finally, the LMCT particles with average size of 15 µm were fabricated.

2.2. Preparation of LMCT/PTFE substrates

To tailor the dielectric properties and mechanical strength of the composite substrates, the sintered LMCT powders were selected as dopant, and mixed into PTFE (China, Dupont) suspension. The main performances of PTFE and LMCT were listed in Table 1.

In this work, F8261 (Japan, TCI Corporation) was chosen as silane coupling agent to optimize the characteristics of ceramic fillers, due to the similar molecule structure between F8261 and PTFE. First, F8261 and un-treated LMCT were weighed on the basis of our previous works. After weighing, F8261 was hydrolyzed in a solvent consisted of alcohol and deionized water with the ambient temperature of 55 °C for 1 h. In this work, the content of F8261 was fixed at 2 wt % of untreated LMCT powders. The volume fraction of deionized water was calculated precisely to guarantee and promote the hydrolysis of F8261. Next, the weighed LMCT powders were poured and blended in hydrolyzed F8261 solution by high speed stirring for 2 h. The homogeneous blend was further baked in drying oven with 120 °C for 3 h. Finally, LMCT powders treated with

Table 1

The performances of LMCT and PTFE.

Properties	PTFE	LMCT
Dielectric constant	2.1	34
Dielectric loss	0.0003	0.0001
Density/(g/cm ³)	2.2	3.43
Thermal expansion coefficient/(10 ⁻⁶ K ⁻¹)	109	7

F8261 were obtained. The schematic processes of surface modification on LMCT powders using F8261 were presented in Fig. 1.

The PTFE suspension and baked LMCT were weighed precisely according to the weight fraction of LMCT/PTFE composites, blended uniformly using high speed stirring for 0.5 h and then baked at 120 °C for 24 h to eliminate organic solvent and water. Thereafter, the baked blend was grinded using high speed grinder. The grinded powder was axially pushed into a square slot model under the pressure of 20 MPa for 30 s. At last, the obtained square slices were fold and baked at 380 °C for 2 h with impressed pressure of 20 MPa.

The crystal phase structure of LMCT particles and LMCT filled substrate composites were recorded by X-ray diffraction (XRD) using CuKa radiation (Philips x'pert Pro MPD, Netherlands). Scanning electron microscopy (SEM, model JEOL JSM-6490) was performed to observe the morphology of cross section of the composite substrates. X-ray photoelectron (XPS, Al, Ka, Thermo Scientific) was used to investigate the surface characterizations of untreated LMCT and modified LMCT powders. Survey scan spectra of untreated and modified LMCT powders were measured range from 0 eV to 1350 eV. In addition, a high resolution scanning on carbon element was operated to observe the carbon character states of LMCT powders. Fourier transform infrared (FTIR, Nicolet 5700) spectra of untreated LMCT together with modified LMCT were also presented to study the chemical bonds on the surface of ceramics. Transmission electron microscopy (TEM, FEI Tecnai G2 F30 S-TWIN, America) was operated to present the morphology of both untreated and modified LMCT powder as well as the interface structure between LMCT and PTFE. The general dielectric properties of PTFE based composites were measured using stripline resonator approach according to IPC-TM-650 2.5.5.5 [24].

3. Results

Fig. 2 shows the XRD pictures of LMCT powder and LMCT/PTFE composites with different weight content of LMCT. XRD characterizations revealed that $Li_2Mg_3TiO_6$ and $CaTiO_3$ (JCPDS # 89–6949) phases coexisted in LMCT. The diffraction peaks appearing at $2\theta = 37.14^{\circ}$, 43.15° , 62.67° , 75.16° and 79.15° were assigned to (111), (200), (220), (311) and (222), respectively. These peaks should belong to the reflections of LMCT powders. Peaks at $2\theta = 17^{\circ}$ and 32° corresponded to PTFE colloform (#JCPDS number 00-054-1595). As shown in Fig. 2, the diffraction peak intensity of PTFE ($2\theta = 17^{\circ}$) experienced a continuous decrease with the further loading of LMCT. On the contrary, the characteristic peak of LMCT located at 62.67° displayed an increasing trend with the filling of LMCT particles. In addition, the peak shape of LMCT powder, indicating the chemical stability of LMCT material.

Fig. 3 presents the survey scan XPS spectra of the untreated LMCT and modified LMCT powders. Peaks at 531, 458, 350, 285 and 49 eV corresponded to O_{1s} , Ti_{2p} , Ca_{2p3} , C_{1s} and Li_{1s} , respectively. The spectrum of modified LMCT powder possessed peaks at 836 and 689 eV, which were not found in untreated LMCT spectrum. Furthermore, these peaks mentioned above were related to the bonding energies of F_{Auger} and F_{1s} , respectively. The observed signals of F_{Auger} and F_{1s} peaks in modified LMCT should be originated from the F element in F8261. The finding indicated that LMCT particles were "covered" by F element after the modification process performed on LMCT using F8261, resulting in a strong hydrophobicity. The presence of F element characteristic peaks confirmed that the functional groups of F8261 have grafted on the surface of LMCT, successfully.

The analyses of XPS narrow scanning on carbon element together with peak fitting on untreated and modified LMCT were shown in Fig. 4. According to the binding energies of the peaks [4],



Fig. 1. Schematics illustration of the interaction between LMCT and F8261.



Fig. 2. XRD patterns of LMCT powder and LMCT/PTFE composites with various weight percentage of LMCT.

the C_{1s} spectra of untreated LMCT and modified LMCT were deconvoluted into six types, and these types were represented by various colored lines: (1) C-F₃, (2) C-F₂, (3) C-F, (4) CO₃²⁻, (5) C_{1s}, (6) C-H (or C). The obtained C_{1s} peak shape of untreated LMCT powders, as shown in Fig. 4(a), was mainly contributed by calibration during the test process. Based on the peak fitting, the C_{1s} peak shape of untreated LMCT was comprised of C-C, C_{1s} and CO_3^{2-} . Obvious changes in C_{1s} peak shape were detected in modified LMCT (Fig. 4(b)) when compared with untreated LMCT (Fig. 4(a)). Meanwhile, the peak fitting analysis was also applied to the spectrum of modified LMCT. It can be concluded from Fig. 4(b) that the main species of C element of modified LMCT were C-F₃, C-F₂, C-F, CO_3^{2-} , C-H (or C) and C_{1s}. Among these species, the observed carbon states of C-C, C_{1s} and CO_3^{2-} were also contributed by the calibration process. The other states of carbon, such as C-F₃, C-F₂, C-F and C-H were probably originated from -(CH₂)-(CF₂)₅-CF₃ chains grafted on the surface of modified LMCT. These detected carbon bonds were from F8261 coupling agent, indicating that the functional groups of



Fig. 3. XPS spectra of (a) untreated LMCT and (b) modified LMCT.

F8261 were successfully transferred to the surface of LMCT particles.

Fig. 5 presents the FTIR patterns of untreated LMCT and modified LMCT powders. The absorption peak at ca. 3650 cm⁻¹ was corresponded to the Ti-OH bond indicating that the surface of LMCT was coated by hydroxyl (-OH). The Ti-OH peak disappeared in the FTIR pattern of modified LMCT. According to Fig. 1, this was due to the reaction between F8261 and LMCT ceramics. The peak at ca. 3640 cm⁻¹ in both patterns were mainly contributed by the ambient moisture during the measure process. Besides, peaks at 1490 cm^{-1} and 1440 cm^{-1} referred to the asymmetric deformation vibration and bending vibration of CO₂, respectively. The CO₂ probably came from the raw materials of Li₂CO₃ and CaCO₃. The peaks at 1250 cm^{-1} was the characterization absorption band (C-F) of F8261, demonstrating that F8261 reacted and grafted on the surface of LMCT powder. Furthermore, peaks at 1140 and 474 cm⁻¹ were correlated with asymmetric stretching vibration and bending vibration of *Si*-O-Ti bond. The absorption band of 667 cm⁻¹ was corresponding to the vibration of Ti-O bond. The existence of Si-O-



Fig. 4. Carbon peak fitting of the XPS narrow scan spectrum of (a) untreated LMCT and (b) modified LMCT: (1) C-F₃, (2) C-F₂, (3) C-F, (4) CO₂²⁻, (5) C₁₅, (6) C-H (or C).



Fig. 5. FTIR spectra of (a) untreated LMCT and (b) modified LMCT powder.

Ti bond confirmed the interaction between F8261 and LMCT again.

As shown in Fig. 6, TEM images were conducted to observe the morphology of both untreated LMCT particles and silane coupling agent modified LMCT particles. Fig. 6(a) depicts the TEM image of untreated LMCT particles, while Fig. 6(b and c) present the TEM images of F8261 modified LMCT particles. It was obvious that the TEM image of the untreated LMCT particles was solid and brunet, while the images of optimized LMCT particles were hazy and lightcolored. The clear distinctions in TEM images were due to that the functional groups of F8261 had transferred and covered the ambient surface of LMCT particles via optimizing procedure [25]. Translucent and hazy films were observed on F8261 modified LMCT powders, as shown in Fig. 6(b and c), which were mainly related to the organic functional groups came from coupling agent. Especially, as shown in Fig. 6(c), the section marked by red oval was corresponded to the entanglement between different optimized LMCT powders. The observed entanglement was primarily contributed by -(CH₂)-(CF₂)₅-CF₃ chains grafted on the ambient of modified LMCT powders.

In this section, the picture of Contact angle was measured to present the hydrophobic nature of F8261 modified LMCT particles. Due to the strong hydrophilic nature, untreated LMCT powders possessed contact angle of near 0° which was consistent with most inorganic ceramics. In other words, the water droplets released during the test were entirely absorbed by untreated LMCT powders when it contacted the samples. However, the hydrophilic characteristics of untreated LMCT particles were changed when the functional groups of F8261 were grafted. Fig. 7 displays the photograph of test droplet on F8261 optimized LMCT specimen. Obviously, the contact angle of F8261 optimized LMCT particles was 156°, representing a strong hydrophobic characteristic. As discussed above, the hydrophobic characteristic of F8261 modified LMCT powders was contributed by the grafted functional groups of $-(CH_2)-(CF_2)_5-CF_3$ which were from F8261. As we known, PTFE was also comprised of $-CF_2-CF_2$ - bonds. Accordingly, it was reasonable to predict that the modified LMCT powders and PTFE could be recombined well.

After the modification process on LMCT powder, the surface of modified LMCT powder possessed the similar molecular structures (-CF₂-CF₂- bonds) as PTFE matrix. The -CF₂-CF₂- bonds on the surface of modified LMCT powders could entangle with PTFE matrix since similar molecular structures significantly promoted the compatibility between modified LMCT and PTFE. To investigate the interface characteristics between modified LMCT particles and PTFE matrix, TEM images of F8261 modified PTFE/LMCT composites were conducted and displayed in Fig. 8. As a comparison, the TEM image of untreated LMCT filled PTFE composite was also attached in Fig. 8(a). As marked, the dark colored solid was LMCT ceramic particles, while the gray colloform was PTFE matrix. Fig. 8(a) shows a bad connection between LMCT and PTFE, while Fig. 8(b) displays a perfect adhesion. Particularly, as shown in Fig. 8(c), the surface of LMCT particle was compactly surrounded by PTFE matrix. There was not even a pore existed in the interface between LMCT and PTFE matrix, representing a strong compatibility and adhesion. This phenomenon directly proved that the modification process on LMCT powders was successful and the compatibility between inorganic LMCT ceramic powders and organic PTFE matrix was greatly promoted.

The cross sectional SEM images of PTFE based and LMCT filled composites were shown in Fig. 9. The weight fraction of LMCT changed from 30 wt % to 70 wt % with a step size of 10 wt %. It can be seen that all specimens exhibited two-phase structure (PTFE and LMCT). We could demonstrate from Fig. 9(a)-9(e) that the PTFE based substrates filled with various content of modified LMCT powders exhibited compact and compatible interfacial microstructure. On the contrary, untreated LMCT filled PTFE composite displayed loose and porous structure. The distinct comparison indicated that the F8261 behaved as a medium between inorganic LMCT and organic PTFE which improved the bonding at the interface region. PTFE completely covered the surface of LMCT particles, especially at low LMCT loading amount. The microstructure of the composites became porous and abrupt with further increasing of LMCT contents, and it was resulted from the lack of PTFE to make



Fig. 6. TEM of LMCT particles (a) untreated LMCT and (b, c) F8261 modified LMCT.



Fig. 7. Contact angle of water droplet on the modified LMCT powders.

sure the liquidity of the composite matrix.

Fig. 10(a) depicts the change of dielectric constant and dielectric loss of PTFE based and LMCT filled composites (around 10 GHz) with increasing the weight fraction of LMCT. Obviously, the dielectric constant of LMCT/PTFE composites was markedly increased by the modification on LMCT particles, while the loss tangent (tan δ) of the composite substrates showed the opposite trend. The optimized dielectric properties of LMCT/PTFE composites were primarily attributed to the modified surface characteristics and compatible connection within the composite matrix which could also be evidenced from Fig. 9. Notably, the PTFE based composite filled with 50 wt % optimized LMCT particles possessed appropriate permittivity of 4.33 and extremely low loss tangent of 0.001.

As reported in previous papers, numerous theoretic models were performed to calculate and predict the dielectric constant of polymer based and ceramic filled substrates. The equations of different models were as follows:

Maxwell-Wagner equation [26]:

$$\varepsilon_{eff} = \varepsilon_c \frac{2\varepsilon_c + \varepsilon_f + 2V_f \left(\varepsilon_f - \varepsilon_c\right)}{2\varepsilon_c + \varepsilon_f - V_f \left(\varepsilon_f - \varepsilon_c\right)}$$
(1)

Lichtenecker equation [27]:

$$\ln \varepsilon_{eff} = V_f \log \varepsilon_f + (1 - V_f) \log \varepsilon_c$$
(2)

Modified Lichtenecker equation [28]:

$$\log \varepsilon_{eff} = V_f (1-k) \log \left(\frac{\varepsilon_f}{\varepsilon_c}\right) + \log \varepsilon_c$$
(3)

where e_f , e_c and e_{eff} were related to the permittivities of LMCT fillers, PTFE and the composites, respectively. The parameter k in Eq. (3) was a fitting factor, and V_f represented the volume fraction of LMCT. Among these assumptive models, it was common for researchers to use the Lichtenecker model (Eq. (2)) to predict their works, which deemed that the fillers were ideal spherical morphology, and were uniformly dispersed into polymer matrix with randomly orientation [17]. Concerning about Modified Lichtenecker model, as reported, k = 0.3 was most optimal for ceramics filled polymers composites. The model of Maxwell-Wagner was usually functioned at low test frequency because the interfacial polarization was prominent at this range.

Fig. 10(b) compared the measured permittivities of LMCT/PTFE composites with theoretical equations mentioned above (around 10 GHz). The measured permittivities of untreated LMCT and optimized LMCT filled composites showed the same trend as that of theoretical values calculated from above discussed models. As



Fig. 8. TEM image of (a) untreated LMCT filled PTFE composite, (b) modified LMCT filled PTFE composites and (c) enlargement of image (b).



Fig. 9. Cross sectional SEM images of LMCT filled PTFE composites (a) 30 wt % (b) 40 wt % (c) 50 wt % (d) 60 wt % (e) 70 wt % (f) untreated LMCT filled PTFE composite.



Fig. 10. (a) Variation of dielectric properties (at 10 GHz) with filler content for $Li_2Mg_{2.88}Ca_{0.12}TiO_6/PTFE$ composites fabricated using untreated and modified $Li_2Mg_{2.88}Ca_{0.12}TiO_6$. Fig. 10(b) Comparison of measured dielectric constant of $Li_2Mg_{2.88}Ca_{0.12}TiO_6/PTFE$ composites with various theoretical models.

shown in Fig. 10(b), the Modified Lichtenecker curve matched well with untreated LMCT filled composites when the filling content of LMCT were 30 wt %, 40 wt % and 50 wt %. Nevertheless, the measured permittivities of untreated LMCT filled PTFE slowly deviated from the values calculated from Modified Lichtenecker equation when the weight fraction of untreated LMCT increased up to 60 wt % and 70 wt %. This deviation was originated from the worse dispersion of LMCT fillers and untight interfacial connection between untreated LMCT particles and PTFE matrix. It is noted that the measured data of the composites filled with F8261 modified LMCT fitted well with Lichtenecker model when the filling contents of modified LMCT were 30 wt %, 40 wt % and 50 wt %. However, as the filling content increased up to 60 wt % and 70 wt %, Maxwell-Wanger model displayed a better consistent with the dielectric constant of F8261 modified LMCT/PTFE composites. Accordingly, the dielectric constant of F8261 optimized LMCT/PTFE composites matched well with Lichtenecker and Maxwell-Wanger model. This was due to the improved surface characteristics of modified LMCT fillers, which resulted in compact connection between LMCT particles and PTFE matrix.

It is well known that the temperature and frequency dependence of permittivities played an increasingly important role in the development of microwave devices design. Fig. 11(a) displays the temperature dependence of permittivities of LMCT/PTFE with the ambient temperature ranged from 30 to 110 °C. The dielectric constant of all the specimens in the study experienced a slight increase with the increasing of temperature. It was due to that the segmental mobility of PTFE in the matrix has been promoted by the raise of temperature, which would improve the polarization of LMCT thereby resulting in an increasing in the dielectric constant



Fig. 11. (a) Variation of dielectric constant with temperature for LMCT/PTFE composites. (b) Variation of dielectric constant with frequency for LMCT/PTFE composites.

[29]. The dielectric constant of all specimens increased less than 2% when the ambient temperature rose from 30 to 110 °C. This phenomenon implied that the permittivities of LMCT/PTFE will not be disturbed by the change of ambient temperature in this range. The frequency dependence of permittivities of LMCT/PTFE respected to different weight fraction of LMCT was shown in Fig. 11(b). For all specimens, the permittivities kept almost constant at the range from 4 GHz to 18 GHz under a given temperature of 30 °C. Furthermore, the plots also displayed that the permittivities of LMCT/PTFE composite substrates increased with the increasing of LMCT filling content.

4. Conclusion

LMCT was modified by F8261, and then loaded in PTFE suspension using high-speed stirring. The surface characteristics of untreated LMCT and F8261 optimized LMCT powders were studied using XPS, FTIR spectra and TEM analyses. It is clear that the functional groups of F8261 grafted and covered the surface of LMCT particles, successfully. Microstructure and dielectric properties of LMCT/PTFE composite substrates were investigated as the weight fraction of LMCT increased from 30 to 70 wt %. The cross sectional SEM morphologies displayed that the ceramic fillers uniformly distributed in PTFE. The dielectric constant of PTFE based and LMCT filled composites increased more or less linearly with the increasing of LMCT content. In addition, the dielectric constant experienced a slight increase as the ambient temperature raised from 30 to 110 °C at 10 GHz. The dielectric constant of modified LMCT/PTFE composites almost remained the same value in the range from 4 to 18 GHz at 30 °C. Furthermore, the dielectric loss of the composites remained relatively low values in different compositions. At last, LMCT/PTFE composite possessed dielectric constant of 4.33 and dielectric loss of 0.001 with 50 wt % LMCT filler loading.

Acknowledgement

This work was supported by National Natural Science Foundation of China (Grant No. 51672038).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2019.06.109.

References

- J. Guo, X. Zhao, T. Herisson De Beauvoir, J.-H. Seo, S.S. Berbano, A.L. Baker, C. Azina, C.A. Randall, Recent progress in applications of the cold sintering process for ceramic-polymer composites, Adv. Funct. Mater. 28 (2018), 1801724.
- [2] H. Peng, H. Ren, M. Dang, Y. Zhang, Z. Gu, X. Yao, H. Lin, The dimensional effect of MgTiO₃ ceramic filler on the microwave dielectric properties of PTFE/ MgTiO₃ composite with ultra-low dielectric loss, J. Mater. Sci. Mater. Electron. (2019) 1–8.
- [3] K.P. Murali, S. Rajesh, O. Prakash, A.R. Kulkarni, R. Ratheesh, Preparation and properties of silica filled PTFE flexible laminates for microwave circuit applications, Compos Part A Appl Sci Manuf 40 (2009) 1179–1185.
- [4] Q. Liu, L. Liu, Y. Ma, C. Zhao, W. Yang, Visible light-induced controlled radical polymerization of methacrylates with perfluoroalkyl iodide as the initiator in conjugation with a photoredox catalyst fac-[Ir(ppy)]₃, J. Polym. Sci. A Polym. Chem. 52 (2014) 3283–3291.
- [5] Y. Zhang, S. Xu, J. Xue, Q. Zhang, Anisotropic mechanical properties and constitutive relations of PTFE coated glass fibers, Compos. Struct. 179 (2017) 601–616.
- [6] W.W. Marzouk, Effect of motion parameters on the tribological behaviour of ptfe-based composite, Compos. Struct. 25 (1993) 193–199.
- [7] H. Peng, H. Ren, M. Dang, Y. Zhang, X. Yao, H. Lin, Novel high dielectric constant and low loss PTFE/CNT composites, Ceram. Int. 44 (14) (2018 Oct) 16556–16560.
- [8] Y. Yuan, Y.R. Cui, K.T. Wu, Q.Q. Huang, S.R. Zhang, TiO₂ and SiO₂ filled PTFE composites for microwave substrate applications, J. Polym. Res. 21 (2014) 366.
- [9] S. Rajesh, K.P. Murali, V. Priyadarsini, S.N. Potty, R. Ratheesh, Rutile filled PTFE composites for flexible microwave substrate applications, Mater. Sci. Eng., B 163 (2009) 1–7.
- [10] K. Murali, S. Rajesh, O. Prakash, A. Kulkarni, R. Ratheesh, Preparation and properties of silica filled PTFE flexible laminates for microwave circuit

applications, Compos Part A Appl Sci Manuf 40 (2009) 1179-1185.

- [11] Z. Li, J. Liu, Y. Yuan, E. Li, F. Wang, Effects of surface fluoride-functionalizing of glass fiber on the properties of PTFE/glass fiber microwave composites, RSC Adv. 7 (2017) 22810–22817.
- [12] L. Zhou, B. Tang, S. Zhang, Influence of Sn-substitution on microstructure and microwave dielectric properties of Na_{1/2}Nd_{1/2}TiO₃ ceramics, J. Mater. Sci. Mater. Electron. 26 (2015) 424–428.
- [13] Z.-x. Fang, B. Tang, F. Si, S.-r. Zhang, Influence of CeO₂ on microstructure and microwave dielectric properties of Na_{1/2}Sm_{1/2}TiO₃ ceramics, J. Mater. Sci. Mater. Electron. 27 (2016) 1913–1919.
- [14] Z. Fang, B. Tang, F. Si, Y. Gong, S. Zhang, Effects of Zr-substitution on microwave dielectric properties of Na_{0.5}Nd_{0.2}Sm_{0.3}Ti_{1-x}Zr x O₃ ceramics (x = 0.00 ~ 0.30), J. Electron. Mater. 45 (2016) 5198–5205.
- [15] Z. Fang, B. Tang, F. Si, S. Zhang, Temperature stable and high-Q microwave dielectric ceramics in the Li₂Mg_{3-x}Ca_xTiO₆ system (x=0.00-0.18), Ceram. Int. 43 (2017) 1682-1687.
- [16] B. Tang, F. Luo, D. Zhou, Y. Yuan, S. Zhang, Effects of CaTiO₃ loading on the properties of PTFE/TiO₂ composites, J. Mater. Sci. Chem. Eng. 5 (2017) 45.
- [17] T.S. Sasikala, M.T. Sebastian, Mechanical, thermal and microwave dielectric properties of Mg₂SiO₄ filled Polyteterafluoroethylene composites, Ceram. Int. 42 (2016) 7551–7563.
- [18] C. Pan, K. Kou, Q. Jia, Y. Zhang, G. Wu, T. Ji, Improved thermal conductivity and dielectric properties of hBN/PTFE composites via surface treatment by silane coupling agent, Compos. B Eng. 111 (2017) 83–90.
- [19] X. Zhang, Y. Ma, C. Zhao, W. Yang, High dielectric constant and low dielectric loss hybrid nanocomposites fabricated with ferroelectric polymer matrix and BaTiO₃ nanofibers modified with perfluoroalkylsilane, Appl. Surf. Sci. 305 (2014) 531–538.
- [20] W. Peng, X. Huang, J. Yu, P. Jiang, W. Liu, Electrical and thermophysical properties of epoxy/aluminum nitride nanocomposites: effects of nanoparticle surface modification, Compos Part A Appl Sci Manuf 41 (2010) 1201–1209.
- [21] Z.-M. Dang, H.-Y. Wang, H.-P. Xu, Influence of silane coupling agent on morphology and dielectric property in BaTiO₃/polyvinylidene fluoride composites, Appl. Phys. Lett. 89 (2006), 112902.
- [22] S.-Y. Wu, Y.-L. Huang, C.-C.M. Ma, S.-M. Yuen, C.-C. Teng, S.-Y. Yang, Mechanical, thermal and electrical properties of aluminum nitride/polyetherimide composites, Compos Part A Appl Sci Manuf 42 (2011) 1573–1583.
- [23] S. Thomas, S. Raman, P. Mohanan, M.T. Sebastian, Effect of coupling agent on the thermal and dielectric properties of PTFE/Sm₂Si₂O₇ composites, Compos Part A Appl Sci Manuf 41 (2010) 1148–1155.
- [24] H. Yue, K.L. Virga, J.L. Prince, Dielectric constant and loss tangent measurement using a stripline fixture, IEEE Trans. Compon. Packag. Manuf. Technol. A B 21 (1998) 441–446.
- [25] L. Ramajo, M. Castro, M. Reboredo, Effect of silane as coupling agent on the dielectric properties of BaTiO₃-epoxy composites, Compos Part A Appl Sci Manuf 38 (2007) 1852–1859.
- [26] Y. Sun, Z. Zhang, C. Wong, Influence of interphase and moisture on the dielectric spectroscopy of epoxy/silica composites, Polymer 46 (2005) 2297–2305.
- [27] J. Krupka, S.A. Gabelich, K. Derzakowski, B.M. Pierce, Comparison of split post dielectric resonator and ferrite disc resonator techniques for microwave permittivity measurements of polycrystalline yttrium iron garnet, Meas. Sci. Technol. 10 (1999) 1004.
- [28] A.H. Sihvola, J.A. Kong, Effective permittivity of dielectric mixtures, IEEE Trans. Geosci. Remote Sens. 26 (1988) 420–429.
- [29] R. Popielarz, C.K. Chiang, Polymer composites with the dielectric constant comparable to that of barium titanate ceramics, Mater. Sci. Eng., B 139 (2007) 48–54.