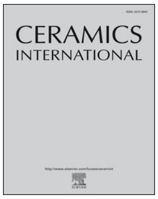
Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Novel high dielectric constant and low loss PTFE/CNT composites

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ARTICLE INFO

Keywords:
A. Sintering
B. Composites
C. Dielectric properties
PTFE

ABSTRACT

Spherical $Ca_{0.55}Nd_{0.3}TiO_3$ ceramic filled polytetrafluoroethylene composites (abbreviated as PTFE/CNT) with different filler volume fractions were prepared. The effects of filler volume fraction on microstructure, dielectric properties and thermal property were studied by scanning electron microscope, vector network analyzer and thermal dilatometer, respectively. The SEM results show that spherical particles are advantageous to reduce the porosity in the interphase which would increase the dielectric loss. Moreover, both the dielectric constant and dielectric loss increased with the increasing volume fraction of CNT microspheres. The high dielectric constant and low dielectric loss composite can be prepared when the ceramic volume fraction is 50 V%: $\varepsilon_r = 12$, $\tan\delta = 8.5 \times 10^{-4}$ (at 10 GHz). Different models were used to predict the dielectric constant of composite, and the effective medium theory shows the least deviation from the experiment. The experimental coefficient of thermal expansions of composites with different volume fractions were less than theoretical data due to the change from loosely bound polymer chain to tightly bound polymer chain which would restrain the coefficient of thermal expansions of composites.

1. Introduction

Ceramic filled polymer composites are been finding increasing applications in electronic packaging applications, 5G mobile communication, large capacity satellite, wearable electronics, etc. since they combine the mechanical flexibility and processing possibility of polymer and outstanding dielectric properties of ceramics [1–3]. Polytetrafluoroethylene (PTFE) possesses nearly lowest dielectric loss ($\tan\delta < 3 \times 10^{-4}$) in polymer family, as well as high chemical stability and high melting point (~320 °C), all of which make PTFE become an ideal choice of polymer matrix [4].

While low dielectric constant could reduce the delay time of electronic signal transmission, high dielectric constant composite ($\varepsilon_r > 10$) was needed to minimize the dimensions of the microwave devices, since the dimensions of the electronic devices are inversely proportional to the square roots of dielectric constants of the materials [5,6]. Whereas, as a kind of polymer, PTFE possesses a low dielectric constant ($\varepsilon_r \sim 2.1$). Thus, high volume fraction of high dielectric constant ceramic was needed to increase the dielectric constant of composite. However, the high volume fraction would bring out the exacerbation of dielectric properties caused by the pores between the agglomerated ceramic particles. In Hu's study, PTFE/$CaTiO_3$ composite showed the best dielectric properties: $\varepsilon_r = 13$, $\tan\delta = 5.3 \times 10^{-3}$ (5 GHz) [4], when the volume fraction of $CaTiO_3$ reached 40 V%. In Jin's studies, PTFE/$SrTiO_3$ composite with 60 wt% $SrTiO_3$ was of high ε_r and low $\tan\delta$: $\varepsilon_r = 12.19$, $\tan\delta = 4.7 \times 10^{-3}$ (9 GHz) [7], and PTFE/BNT composite with 70 wt% BNT was of high ε_r and low $\tan\delta$: $\varepsilon_r = 10.56$, $\tan\delta = 4 \times 10^{-3}$ (11.5 GHz) [8]. From the previous studies we can know that composite with high dielectric constant can be obtained at high ceramic fraction while the low dielectric loss ($\tan\delta < 1 \times 10^{-3}$) will be difficult to be maintained. Thus, the research of composite with both high dielectric constant and low dielectric loss is still a challenge.

$Ca_{0.55}Nd_{0.3}TiO_3$ (CNT) ceramic possesses both high dielectric constant ($\varepsilon_r \sim 100$) and low loss tangent (5.5×10^{-4}, 3 GHz). And the spherical particles are advantageous to increase the ceramic volume fraction [2]. Hence, in this paper, PTFE and spherical CNT were chosen as polymer matrix and ceramic filler, respectively. The effects of ceramic volume fraction on microstructure, dielectric properties and coefficient of thermal expansion had been fully studied.

2. Experimental procedure

CNT ceramic powders were prepared by the conventional solid state reaction method. The raw materials $CaCO_3$ (99.9%), Nd_2O_3 (99.9%) and TiO_2 (99.9%) were weighed according to the desired stoichiometry of $Ca_{0.55}Nd_{0.3}TiO_3$. The powders were ball milled by ZrO_2 balls in deionized water medium for 24 h. The slurry was dried at 150 °C for 5 h and then the powders were calcined at 1150 °C for 4 h. Afterwards, the

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https://doi.org/10.1016/j.ceramint.2018.06.077
Received 10 May 2018; Received in revised form 8 June 2018; Accepted 10 June 2018
0272-8842/

Please cite this article as: Peng, H., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.06.077

calcined powders were secondary ball milled, spray granulated to obtain spherical particles and sintered at 1300 °C for 4 h. Again, the powders were finely ground and sieved using 75-μm sieves. The sintered powders were treated by 1 wt% gamma-aminopropyl triethoxysilane (KH550). To modify the surface of ceramic powders, the KH550 (1 wt% of the ceramic powders) was hydrolyzed in 95 wt% aqueous ethanol solution. After that, the ceramics were dispersed in the solution and mixed by magnetic stirring for 2 h. The slurry was dried at 80 °C for 10 h to obtain the treated ceramic powders.

The PTFE/CNT composites were prepared by mold pressing and sintering the mixture of polytetrafluoroethylene (PTFE, Daikin) and CNT powders. PTFE and different volume fractions of CNT (V_f) were mixed for 1 h by three-dimensional mixing machine. The mixture was preformed under uniaxial pressure of 50 MPa for 10 min. Finally, the green compact was heated to 360 °C with a heating rate of 5 °C/min and soaked for 2 h.

The archimedes' method was used to measure the bulk densities of ceramics. The microstructure of CNT ceramic was examined by a Magellan 400 field emission scanning electron microscope. The method developed by Hakki and Coleman was used to measure the microwave dielectric properties of the samples. All the microwave measurements were used in the TE_{011} mode of an Agilent E8363A PNA series network analyzer (10 GHz). The coefficient of thermal expansion (CTE) was measured by Netzsch DIL 402 C with a heating rate of 5 °C/min from 25 °C to 100 °C. And the moisture absorption was measured according to IPC-TM-650 2.6.2 standard.

3. Results and discussions

The micro-morphology and dispersion of ceramic filler in PTFE matrix were studied by using SEM technique, and the cross sectional SEM images of composites filled with different volume fractions (10 V%, 30 V%, 50 V%, 70 V%) of CNT ceramics are shown in Fig. 1. Obviously, the CNT ceramic fillers are microsphere with an average size of 40 μm and disperse in PTFE matrix. Otherwise, there are few pores in composite at lower ceramic volume fractions. By comparison, at higher volume fractions ($V_f \geq 50$ V%), particles begin to agglomerate which results in the formation of pores between particles. To investigate the influence of spherical particles on microstructure. The cross sectional SEM images of PTFE filled with spherical and non-spherical particles ($V_f = 50$ V%) are shown in Fig. 2. Apparently, compared with non-spherical particles, spherical particles are advantageous to reduce the porosity and making microstructure more compact.

Fig. 3 shows the experimental and theoretical densities of PTFE/CNT composites with different volume fractions of CNT fillers (0–70 V%). The theoretical density (ρ_{theo}) of composite was calculated by the mixture rule [9]:

$$\rho_{theo} = (1-V_f)\rho_m + V_f\rho_f \tag{1}$$

where the ρ_m and ρ_f represent the densities of matrix and filler respectively, and the V_f represent the volume fraction of the filler. The densities of PTFE and CNT ceramic measured by Archimedes method were 2.17 g/cm^3 and 4.93 g/cm^3 respectively. Thus, due to the higher density of ceramic filler, the experimental and theoretical densities of composites increased steadily with the increasing volume fraction of CNT ceramic. However, the experimental density curve started to deviate from the theoretical one when the filler volume fraction reached 40 V%. This may be attributed to the existence of pores which originated from the agglomeration of the fillers. In this three phases system (matrix, filler, pore), the porosity (p) can be calculated using the following equations [10]:

$$\rho_{rel} = \rho_{exp}/\rho_{theo} \tag{2}$$

$$\rho_{exp} = \rho_{rel}(1-p)+\rho_{pore}p \tag{3}$$

Where ρ_{exp} and ρ_{rel} represent the experimental and relative densities respectively, ρ_{pore} represents the density of pores which was regarded as 0 in this system. The results are shown in Table 1. Obviously, a lower filler volume fraction produced a denser structure. However, with the increasing of filler volume fraction, the relative density decreased,

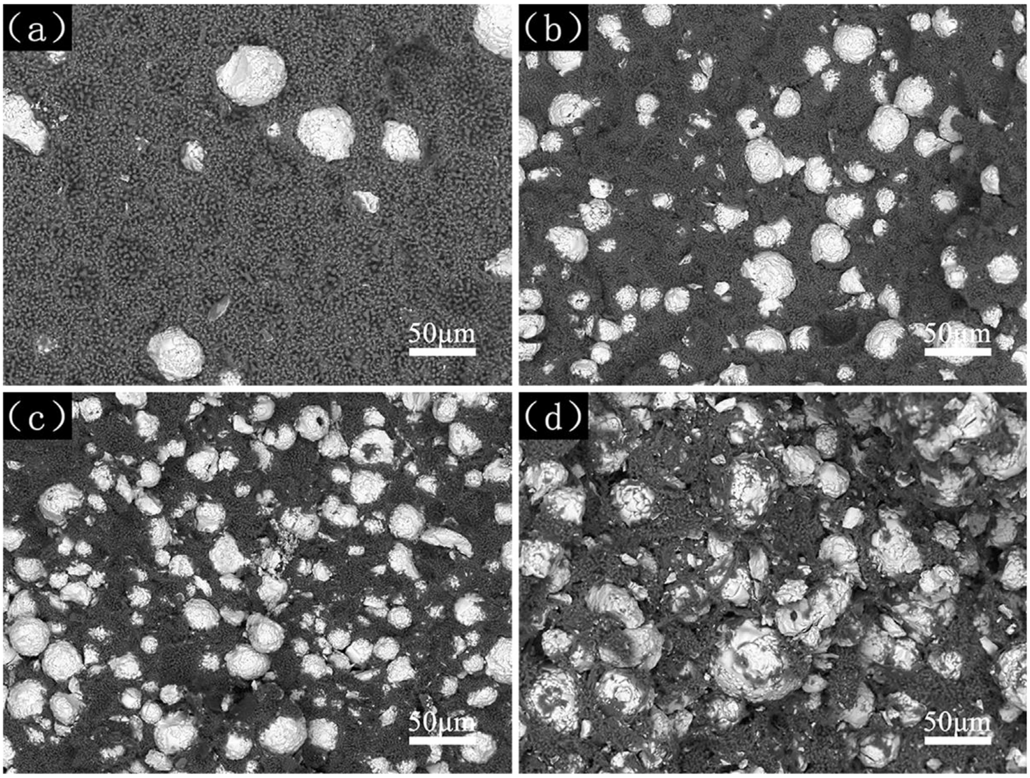

Fig. 1. Cross sectional SEM images of PTFE/CNT composites with different volume fraction of CNT ceramics: (a)10 V%, (b)30 V%, (c)50 V%, (d)70 V%.