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Fabrication and characterization of micro-nano AlN co-filled PTFE composites with enhanced thermal conductivity: a morphology-promoted synergistic effect

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Abstract In this study, micro-nano AlN co-filled PTFE composites were prepared by powder processing technique to obtain high performance electronic packaging materials with high thermal conductivity and outstanding thermal stability. The synergistic effect of micro-size and nano-size AlN particles on the thermal, mechanical, dielectric properties of the composites is systematically investigated. The SEM images indicate that nano-size AlN particles are filled into the interspaces between micro-size AlN particles, resulting in a tightly stacked structure in the composites. Compared with the PTFE composites with single-size AlN, the composites filled by 0.3 V_f micro-nano AlN display higher thermal conductivity (0.84 W/mK), and the thermal stability and mechanical properties of the composites are also enhanced. Meanwhile, the composites exhibit excellent dielectric properties: the maximum dielectric constant is 4.4 and dielectric loss is 0.0035 at 100 Hz.

1 Introduction

With the rapid development of the electronics industry, electric devices tend to be integration, miniaturization and functionalization. However, the accumulation of self-generated heat and a rise in temperature during operation may lead to premature [1–4]. So far, materials for electronic packaging materials should have high thermal conductivity to dissipate heat. Nevertheless, a low dielectric constant is required to avoid signal propagation delay and a low dielectric loss is required to reduce signal attenuation [5, 6]. Ceramic/polymer composites can combine easy processing of polymers and high thermal conductivity of ceramics. Due to this fact, they are promising candidates for semiconductor devices packaging.

Compared to epoxy resin, the most widely used polymer matrix, polytetrafluoroethylene (PTFE) exhibits outstanding properties, such as excellent dielectric properties, chemical inertness and low water absorption, especially high thermal stability [7, 8]. In our previous work [9], we studied the dielectric, mechanical properties and thermal stability of AlN/PTFE composites, but the thermal conductivity remains not to be discussed.

To improve the thermal conductivity of polymeric composites, a large amount of ceramic fillers (generally more than 50 vol.%) should be incorporated into the polymer matrix, which in turn deteriorates processibility and mechanical properties of polymeric composites seriously [10, 11]. Recently, several researches [12–15] have reported that combinations of fillers with different sizes could effectively enhance the thermal conductivity of the

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composites. The hybrid fillers can build a more compactable thermal conductive network and improve the thermal conductivity of the composites at a relatively low content.

In the present study, micro-nano AlN co-filled PTFE composites are prepared by cold pressing followed by sintering. AlN is chosen as the filler due to its high thermal conductivity and relatively low dielectric constant [16]. As far as we know, no one has reported this method used in PTFE composites before. The synergistic effect of micro-size and nano-size AlN particles on the thermal, mechanical, dielectric properties of the composites will be systematically discussed.

2 Experimental

2.1 Materials

Polytetrafluoroethylene, powdery, was purchased from Jinan 3F Fluorin-chemical (Shandong, China). Micro-size AlN powder with average size in 2 µm was provided by Xi'an global chemical instrument company (Xi'an, China), while nano-size AlN particles with an average diameter of 50 nm were purchased from Hefei Kaier Nanotechnology (Anhui, China). Acetone was supplied by Jingzhou Jiangshan fine chemical Ltd (Jingzhou, China).

2.2 Preparations

For comparison, two kinds of composites were prepared. One is the micro-nano AlN filled composites (the volume ratio of micro-size and nano-size AlN is 9:1), and the other one is micro-size AlN filled composites. The PTFE composites were prepared as follows. Firstly, various volume fractions (0.1–0.3 V_f) of AlN particles and PTFE powder were dispersed in acetone using an ultrasonic mixer. The mixture was heated to 120 °C for 2 h to get dry powders. Secondly, the dried powders were cold pressed into specimens at pressure of 50 MPa. Finally, the compact samples were heated to 375 °C at a rate of 1 °C/min and then soaked for 2 h. The cooling process was 1 °C/min from 375 to 255 °C and then specimens cooled in the furnace naturally.

2.3 Characterization

Tensile strength of composites was obtained according to HG/T 2902-1997. Drawing speeding was 100 mm/min. In each system, more than five specimens were tested. The hardness of the samples was texted by Shore D durometer. An average of six reading was taken for each specimen. The morphology of fractured cross sections of composites was observed via using scanning electron microscopy (SEM, VEGA3 LMH). Before observation, samples were ruptured in liquid nitrogen, and the surface was sprayed a thin, even film of gold. Differential scanning calorimetry (DSC, Q1000, TA instrument) was used to record the melting curves of PTFE and PTFE composites at a heating rate of 10 °C/min under N_2 from room temperature to 380 °C. Thermo-gravimetric analysis (TGA, Q600, TA instrument) was employed to determine the thermal stability of composites at a heating rate of 10 °C/min under N_2 from room temperature to 800 °C. The dielectric properties of composites were characterized using a Novocontrol dielectric spectrometer from 100 Hz to 1 MHz. The samples were about 2 mm in thickness, 30 mm in diameter. Prior to characterization, both sides of circular samples were evaporated with thin gold layers. The thermal diffusivity (λ) and specific heat(C) were measured by the lasher flash method (Netzsch, LFA447, Germany) on square specimens (10 × 10 mm, about 1 mm in thickness). The density (ρ) of specimen was measured by Archimedes method [17]. The thermal conductive coefficient (λ) was calculated from the equation:

$$\lambda = \delta \times C \times \rho \tag{1}$$

3 Results and discussion

3.1 Morphology of PTFE and PTFE composites

Figure 1 shows the SEM micrographs of PTFE and PTFE composites. The cross-section of pure PTFE presents a relatively smooth surface. For the composites, AlN particles are dispersed uniformly in the PTFE matrix and the packing of the particles grows denser with the content of AlN increases. For the composite sample with 0.1 V_f micro-nano AlN, the internal structure of composites presents a typical sea-island structure. AlN particles are isolated by PTFE matrix and can't connect with each other. While for the composite sample with 0.3 V_f micro-nano AlN, the distance between micro-size AlN particles becomes very small and the interconnection among them can be found easily. Seen from the image with higher magnification (Fig. 1d), there are still a lot of interspaces between neighboring micro-size AlN. Nano-size AlN particles can be found filled into the gaps of micro-size AlN particles, resulting in a more compact morphology.

Figure 2 shows the elements mapping of AlN/PTFE composites. The green dots which represent the element of Al indicate the distribution state of AlN in the composite. It can be seen that AlN particles randomly and uniformly disperse among the PTFE matrix.

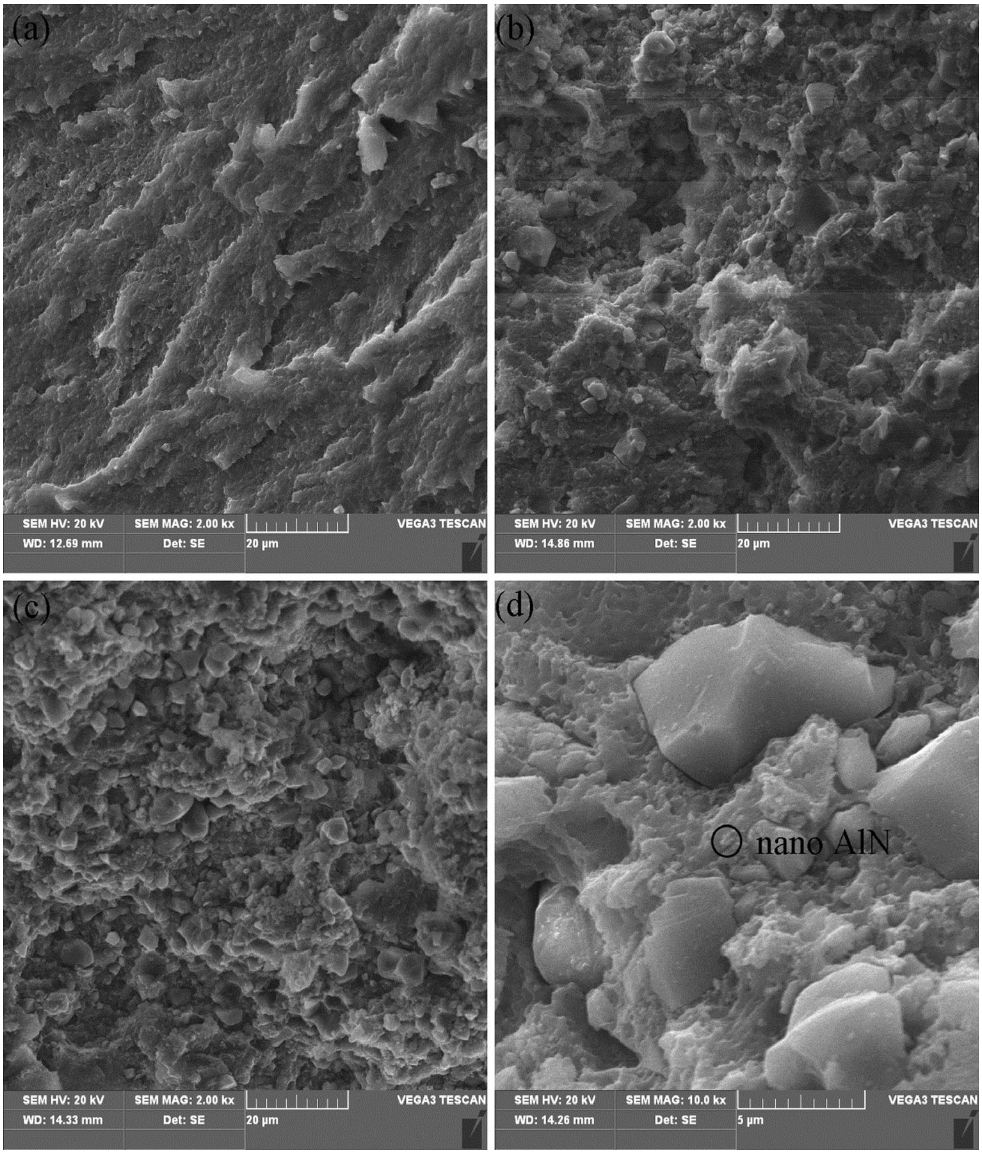

Fig. 1 SEM micrographs of **a** PTFE, PTFE filled by **b** $0.1V_f$ micro-nano AlN, **c**, **d** $0.3V_f$ micro-nano AlN at different magnifications

3.2 Melting temperature and degree of crystallinity

As a kind of semicrystalline polymer, the melting temperature (T_m) of PTFE is an important property because it is the maximum application temperature of the resin. What's more, the degree of crystallinity (X_c) has an important effect on the thermal conductivity of PTFE because the thermal conductivity of the crystalline phase is higher than that of the amorphous phase [18]. Melting behavior of PTFE and PTFE composites was evaluated by DSC(Fig. 3). The melting temperature and the degree of crystallinity are showed in Table 1. X_c was measured by the ratio of the measured fusion heat, ΔH_m to that of a 100 % crystalline PTFE, ΔH_m^{∞} (69 Jg^{-1}) [19]:

$$X_c = \frac{\Delta H_m}{\Delta H_m^{\infty}(1-\alpha)} \tag{2}$$

where α was the weight fraction of AlN in the composites. It can be seen that the melting temperature of PTFE composites was almost independent on the AlN loading. While the calculated X_c exhibits a weak dependence on the AlN loading and shows a slight diminishing trend with increasing filler content, which due to the obstructed mobility of PTFE chains. It also can be seen that the X_c of composites filled by micro-nano AlN is higher than that filled by micro-size AlN, which can be interpreted by the heterogeneous nucleation effect [20] of nano-size AlN during the crystallization process.

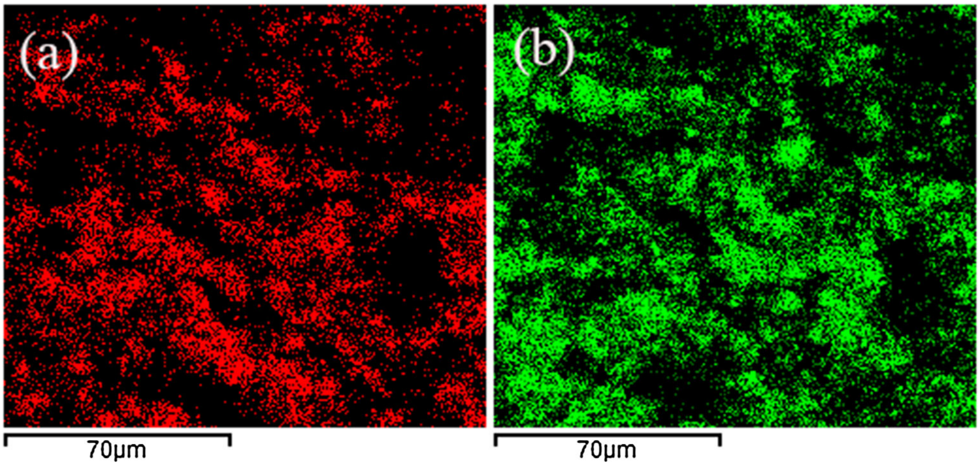

Fig. 2 Elements mapping of AlN/PTFE composites. **a** the *red dots* represent the element of F, **b** the *green dots* represent the element of Al (Color figure online)

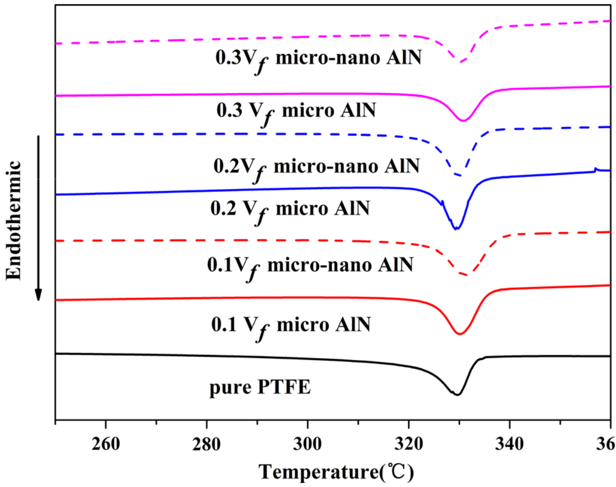

Fig. 3 DSC traces of neat PTFE and AlN/PTFE composites with various filler content as indicated below each *curve*

3.3 Thermal conductive properties of PTFE and PTFE composites

Figure 4 shows the thermal conductivity curves of composites incorporated with micro-size AlN and micro-nano AlN. All composites show an enhancement in thermal conductivity with the increase of AlN. The thermal conductivity of composites improves slowly at low filler content. As the filler content further increases, the thermal conductivity of composites increases rapidly. Interestingly, the composite filled by micro-nano AlN exhibits higher thermal conductivity compared to that of micro-size AlN especially at high filler content. For example, the thermal conductivity of the composites filled by 0.3 V_f micro-nano AlN (0.84 W/mK) is much higher than that of the composites filled by 0.3 V_f micro-size AlN (0.7 W/mK). The phenomenon can be explained by the distribution state of filler in the polymer matrix [21]. As shown in Fig. 5, when the content of AlN particles filled into PTFE matrix is low, the internal structure of composites is typical sea-island structure. Either micro-size AlN particles or nano-size AlN particles are isolated by PTFE matrix, which inhibits the formation of thermal conductive paths, thus the deviation of thermal conductivity between composites filled by micro-size AlN and micro-nano AlN is small. With the increase of filler, micro-size AlN particles begin to connect with each other. But the interspaces between them suppress the formation of thermal conductive networks in the composites. Nano-size AlN particles are filled into the gaps between micro-size AlN particles because they are prone to get closer each other due to high surface energy [12]. So nano-size AlN particles can play a role as a bridge-link action between micro-size AlN particles, facilitating the formation of thermal conductive networks.

There are many theoretical models having been developed to predict the thermal conductivity of polymer composites. In this study, Maxwell model [22] is used to investigate AlN/PTFE composites. Maxwell model:

Table 1 Thermal data of pure PTFE and PTFE composites from DSC analysis

	Micro-size AlN (volume fraction)				Micro-nano AlN (volume fraction)		
AlN content	0	0.1	0.2	0.3	0.1	0.2	0.3
T_m (°C)	329.7	330.1	329.3	330.8	331.2	329.8	330.4
X_c (%)	31.6	30.8	29.8	29.5	34.7	34.2	30.5

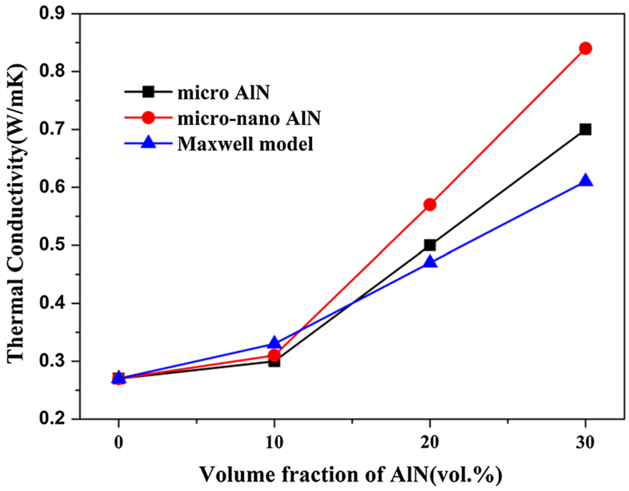

Fig. 4 Thermal conductivity curves of PTFE and AlN/PTFE composites

$$k_c = k_m \frac{k_f + 2k_m + 2v(k_f - k_m)}{k_f + 2k_m - v(k_f - k_m)} \tag{3}$$

where k_c, k_f and k_m are the thermal conductivity of the composite, filler and the matrix, respectively, v is the volume fraction of the filler.

As shown in Fig. 4, we can see that at low filler loading, the predicted value is a little higher than the experimental value. This can be ascribed to that Maxwell model doesn't consider the interfacial thermal resistance, which is caused by various types of phonon scattering processes. While Maxwell model seriously underestimates thermal conductivity of composites at high filler content. This is due to Maxwell model is based on the assumption that filler particles are randomly distributed and non-interacting spheres. Thus Maxwell model is not suitable for predicting the thermal conductivity of composites with high filler loading.

The temperature dependence of the thermal conductivity of pure PTFE and composites filled by different micro-nano AlN content is showed in Fig. 6. We can see that the thermal conductivity of pure PTFE increases slightly with increasing temperature, while the thermal conductivity of PTFE composites shows a decreasing trend and the decreasing trend becomes more and more significant as the filler content increases. It is proposed that there are two competing mechanisms for temperature affecting the thermal conductivity of composites. On one hand, increasing temperature would improve the segmental mobility of polymer, which facilitates lattice vibration or phonon transport, thereby leading to an increase in thermal conductivity. On the other hand, the volume of composites expands when heated because of the high thermal expansion coefficient of PTFE matrix, which results in increasing

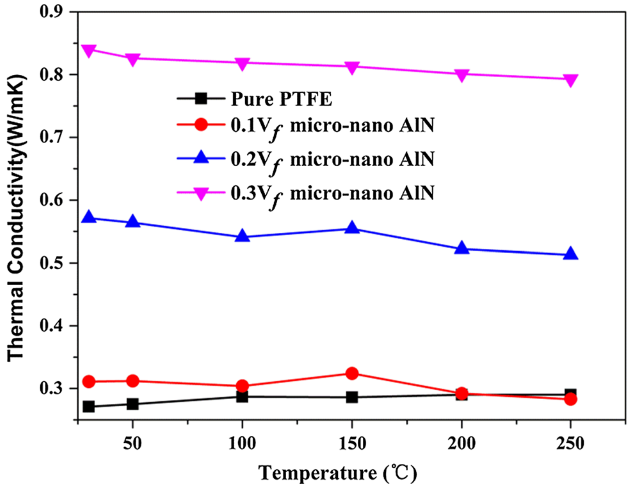

Fig. 6 Temperature dependence of the thermal conductivity of pure PTFE and composites filled by different micro-nano AlN content

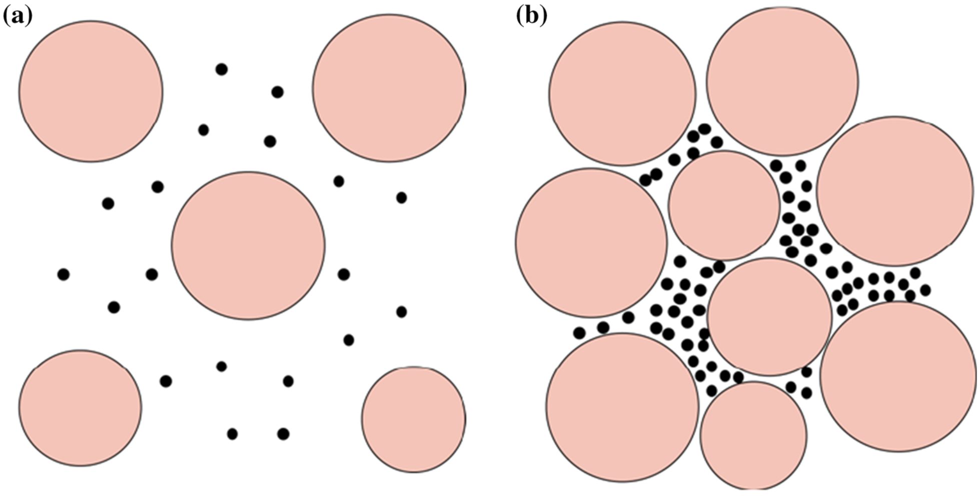

Fig. 5 Schematic diagrams of internal structure of the composite: **a** low filler content, **b** high filler content

distance of adjacent AlN particles and destroying thermal conductive pathways, thus leading to a decreased thermal conductivity. For pure PTFE, there is only the first mechanism. For PTFE composites, both mechanisms influence the thermal conductivity, but in the present case the thermal expansion is the dominant mechanism.

3.4 Mechanical properties of AlN/PTFE composites

Figure 7a shows the variation of tensile strength of PTFE and PTFE composites as a function of AlN volume fraction. The tensile strength of PTFE composites filled by either micro-size or micro-nano AlN shows a decreasing trend with increasing filler content. This result is due to the fact that the fillers serve as stress-concentration points and inner defects such as pores are introduced into the composites [23]. Nano-size AlN particles are prone to embed in the holes between PTFE and micro-size AlN particles, which accordingly decrease defects. Thus, the tensile strength of PTFE composites filled by micro-nano AlN is higher than that filled by micro-size AlN. Figure 6a also suggests that, at 0.3 V_f of micro-nano AlN, the composites still reserve good tensile strength, i.e. 9.4 MPa.

Figure 7b shows the effect of AlN content on the shore D hardness of AlN/PTFE composites. It can be seen that the hardness of two kinds of composites increase with increasing AlN content monotonously, which can be ascribed to that AlN particles have much higher hardness than PTFE matrix. Similarly, nano-size AlN particles could fill into the interspaces of micro AlN particles, which makes the load almost forced on rigid micro-size and nano-size AlN particles [24] and leads to higher shore hardness of the composites filled by micro-nano AlN.

3.5 Frequency dependence of dielectric properties of AlN/PTFE composites

The signal propagation delay in an integrated circuit is determined as the following equation [6]:

$$T_d = \frac{l}{c}\sqrt{\varepsilon_r} \tag{4}$$

where c is the velocity of light, l is the transmission distance of the signals and ε_r is the relative dielectric constant of the packaging material. From the equation, we can conclude that a high dielectric constant results in longer delay time. The frequency dependence of dielectric constant is shown in Fig. 8a. It can be seen that the dielectric constant of all composites are almost independence on frequency and they keep at a low level, for example, the maximum dielectric constant is 4.4. The excellent frequency stability of the dielectric constant is due to the non-polarity and intrinsic weak frequency dependence of PTFE matrix. As the filler content increases, there is a gradual increase in the dielectric constant, which is due to that dipole–dipole interaction within the powders leads to the average electric filed enhancement in PTFE matrix. The dielectric constant of composites filled by micro-nano AlN is higher than that of micro-size AlN, which can be ascribed to that the bridge-link action of nano-size AlN will enhance dipole–dipole interaction between micro-size AlN particles.

Figure 8b presents the frequency dependence of dielectric loss tangent. The dielectric loss tangent is mainly associated with interfacial polarization at low frequency, while dielectric relaxation is dominant at high frequency [21]. We can see that the dielectric loss tangent of PTFE

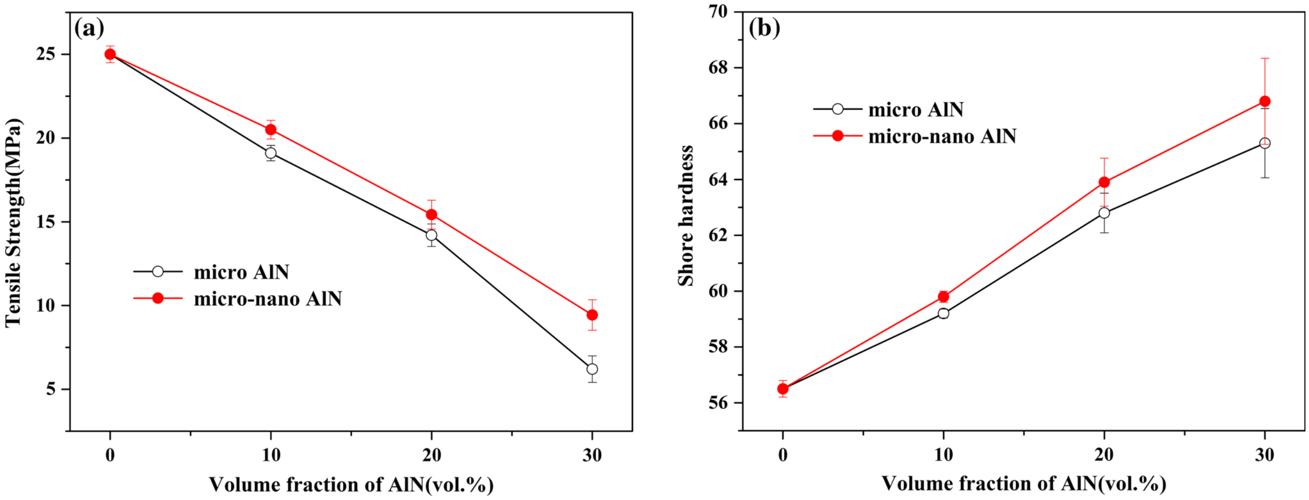

Fig. 7 The tensile strength (**a**) and shore D hardness (**b**) of PTFE and PTFE composites

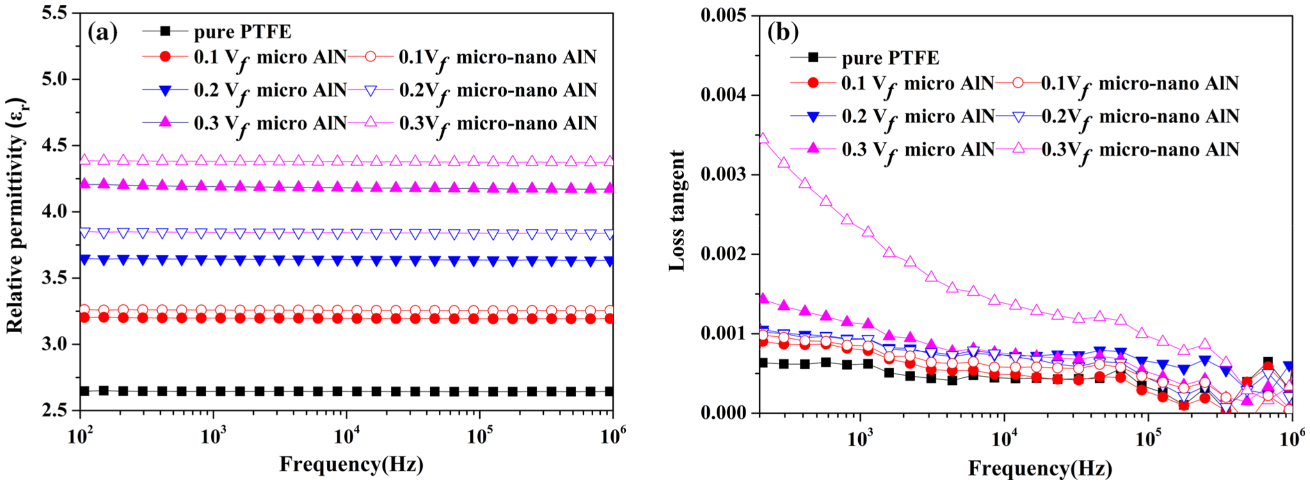

Fig. 8 Frequency dependence of the dielectric constant (**a**) and dielectric loss tangent (**b**) of pure PTFE and composites

composites with AlN filler (<0.2 V_f) are weakly dependent on the measured frequency. As the frequency increases, the rapid decrease of the dielectric loss tangent of the composites with 0.3 V_f micro-nano AlN may be due to that the interfacial dipoles have less time to orient themselves in the direction of the alternating field [25]. The higher dielectric loss tangent of composites filled by micro-nano AlN can be explained as follws. The higher specific surface of nano-size AlN can introduce much more interfacial area into the composites, which will enhance the interfacial polarization. The dielectric loss tangent tends to increase near 1 MHz, which is related to the dielectric relaxation process of PTFE matrix. In general, the dielectric loss tangent of composites remains a very low level, i.e., the maximum dielectric loss tangent is 0.0035 at 100 Hz.

3.6 Thermal stability of AlN/PTFE composites

Thermo-gravimetric analysis curves of pure PTFE and PTFE composites are presented in Fig. 9. It can be seen that the weight of pure PTFE and PTFE composites is relatively stable below 500 °C, which can be attributed to the intrinsic high thermal stability of PTFE matrix. It also can be seen that the thermal decomposition temperature at 5 % of weight loss (T_{d5}) of the composite filled by 0.3 V_f micro-size AlN (523.4 °C) is little higher than that of the pristine PTFE (521.9 °C), while T_{d5} of the composite filled by 0.3 V_f micro-nano AlN (536.9 °C) is much higher. This implies that the incorporation of micro-nano AlN is more beneficial to enhance the thermal stability of PTFE composites. The enhancement of thermal stability of the composites may be ascribed to two factors: (1) during thermal decomposition, thermal motion of PTFE segments near the surfaces of nano-size AlN particles will be restricted due to the physical interlock [26]; (2) the composites filled by micro-nano AlN with higher thermal conductivity will help the heat transfer and avoid local overheating [27], thus reduce the decomposition of composites. In addition, the actual residual mass values of two composites (38.21 %, 37.24 %) are in good agreement with theory residual mass value (39.05 %), which suggests that the filler disperses uniformly among the PTFE matrix.

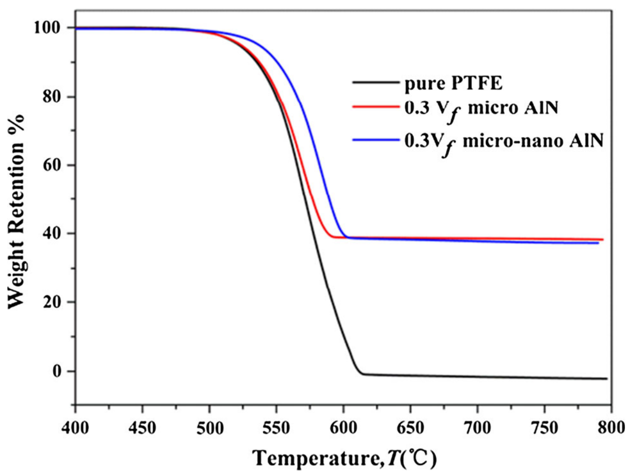

Fig. 9 TGA curves of neat PTFE and PTFE composites filled by 0.3 V_f micro AlN and 0.3 V_f micro-nano AlN

4 Conclusions

By combining micro-size AlN and nano-size AlN particles, a synergistic effect of micro-size and nano-size AlN particles on the thermal, mechanical, dielectric properties of AlN/PTFE composites was achieved. Compared to micro-size AlN, the presence of nano-size AlN provided higher thermal conductivity. This should be ascribed to the bridge-link action of nano-size AlN particles. Meanwhile, the mechanical properties and thermal stability were promoted. The dielectric constant and dielectric loss tangent maintained a low level within a wide frequency range. The excellent dielectric properties as well as thermal properties made the composites a promising application for electronic packaging and thermal management in semiconductor devices.

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