

## Effect of Calcination Temperature of TiO<sub>2</sub> on the Crystallinity and the Permittivity of PVDF-TrFE/TiO<sub>2</sub> Composites

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**ABSTRACT:** Composite membranes of poly(vinylidene-trifluoroethylene)/titanium dioxide (PVDF-TrFE/TiO<sub>2</sub>) were prepared by the solution cast method. The crystallization behavior and dielectric properties of the composites with TiO<sub>2</sub> calcined at different temperatures were studied. Transmission electron microscopy and X-ray diffraction (XRD) results showed that the TiO<sub>2</sub> nanoparticles calcined at different temperatures were well dispersed in the polymer matrix and did not affect the structure of the PVDF-TrFE matrix. XRD and differential scanning calorimeter measurements showed that the crystallinity of PVDF-TrFE/TiO<sub>2</sub> composites increased as the addition of TiO<sub>2</sub> with different calcination temperatures. The dielectric property testing showed that the permittivity of PVDF-TrFE/TiO<sub>2</sub> membrane increased rapidly with the increase of TiO<sub>2</sub> content and the calcination temperature of TiO<sub>2</sub> at constant TiO<sub>2</sub> content, but the dielectric loss did not change much. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 296–300, 2013

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### INTRODUCTION

Polymer composites with high permittivity and low dielectric loss have attracted much attention because of their applications in capacitors, actuators, and sensors.<sup>1–3</sup> Traditional polymers are light-weight, flexible, and easily integrated. However, most pure polymers show a relatively low permittivity in the range of 2–5.<sup>4</sup> Ferroelectric ceramics have very high dielectric permittivity but are brittle and hard to fabricate.<sup>5,6</sup> One effective way to obtain high-performance materials is to combine ceramics with polymers to form organic–inorganic composites. The composites have high permittivity, low dielectric loss, and good flexibility. Many researchers have focused on the study of the structures, crystallization properties, and dielectric properties of the composites.<sup>7–9</sup>

Poly(vinylidene fluoride) (PVDF) and its copolymer poly(vinylidene-trifluoroethylene) (PVDF-TrFE), have been studied for many years because of their good mechanical, ferroelectric, and piezoelectric properties.<sup>10–13</sup> PVDF is a semicrystalline polymer with five kinds of phases according to crystallization conditions. The most studied phases are the nonpolar  $\alpha$ -phase with trans-gauche conformation, polar  $\beta$ -phase with all-trans conformation, and polar  $\gamma$ -phase with trans-trans-trans-gauche conformation.<sup>14</sup> The  $\beta$ -phase shows dielectric, piezoelectric, and ferroelectric properties, leading to high permittivity<sup>15</sup>; however, the most

common phase in PVDF is the nonpolar  $\alpha$ -phase. The  $\beta$ -phase is required for high permittivity. By introducing a second unit, such as TrFE, the  $\beta$ -phase can be obtained. It is known that the copolymer PVDF-TrFE with 20–50 mol % TrFE favors the  $\beta$ -phase and exhibits ferroelectric to paraelectric (F-P) phase transition below the melting point ( $T_m$ ).<sup>16</sup> The crystallinity, ferroelectricity, dielectric properties and energy storage of PVDF-TrFE have been widely studied.<sup>17–19</sup>

Titanium dioxide (TiO<sub>2</sub>) is one of the most widely used metal oxides in sensors and semiconductors. Its various phases all have a relatively large permittivity. For example, the rutile phase has a permittivity of 114, and the anatase phase of TiO<sub>2</sub> has a permittivity of 31.<sup>20</sup> The phase of TiO<sub>2</sub> is determined by the calcination temperature during preparation. With the increase of calcination temperature, the phase tends to rutile, which has a higher permittivity than anatase. If properly modified, TiO<sub>2</sub> can be homogeneously dispersed in the polymer matrix and can have interfacial interactions with the polymer matrix.<sup>21,22</sup>

In this study, membranes of PVDF-TrFE/TiO<sub>2</sub> were prepared with different contents of TiO<sub>2</sub> nanoparticles by the solution cast method. The TiO<sub>2</sub> nanoparticles were made by the sol-gel method. TEM, XRD, differential scanning calorimeter (DSC), and dielectric testing were used to characterize the properties of the composite membranes. The effect of the calcination

temperature of TiO<sub>2</sub> on the crystallization behavior and dielectric properties of the composite membranes were studied. The results showed that both the crystallinity and the permittivity of the composites improved significantly with the increase of calcination temperature of TiO<sub>2</sub>.

## EXPERIMENTAL

### Materials

PVDF-TrFE (70–30 mol %) was purchased from Piezotech (Hésingue, France). Tetrabutyl titanate (TBOT) and dimethyl formamide (DMF) were bought from Sinopharm Chemical Reagent (China). Polyethylene glycol (PEG200) was bought from Tianjin Guangfu Fine Chemical Research Institute (China). Hydrochloric acid and ammonium hydroxide were purchased from Beijing Chemical Works (China).

### Sample Preparations

TiO<sub>2</sub> nanoparticles were prepared from TBOT by a modified sol-gel method.<sup>23</sup> 5 g of TBOT was dissolved in ethanol; 3.8 mL of hydrochloric acid, and 1 g of the surfactant PEG200 were added. The mixture was stirred at ambient temperature for 3 h, and the pH of the solution was adjusted to 7 by adding ammonia dropwise. The solution was let stand for 24 h, and the sol was washed by deionized water and ethanol. The gel was dried at 80°C for 10 h and then calcined at 450°C and 850°C for 3 h to obtain TiO<sub>2</sub> nanoparticles.

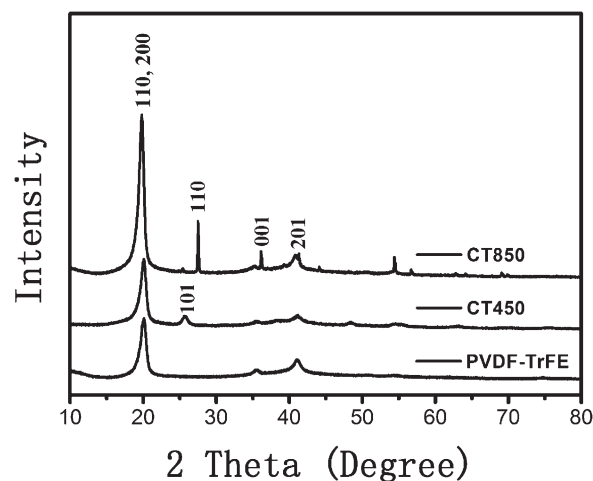
PVDF-TrFE/TiO<sub>2</sub> composite membranes were prepared by the solution cast method. Predetermined amounts of TiO<sub>2</sub> nanoparticles, polyvinyl pyrrolidone (PVP) and PVDF-TrFE were ultrasonically dispersed in DMF for 2 h until they are well dispersed in the solution. Then the solution was stirred vigorously for 4 h. Afterward, the solution was poured into a tank, which was then put into an oven at 80°C for 10 h to evaporate the solvent. After cooling down to ambient temperature, the content of the tank was annealed at 120°C for 4 h. Membranes with an average thickness of 100–120 μm were made. In the discussion below, the PVDF-TrFE/TiO<sub>2</sub> composites with TiO<sub>2</sub> calcined at 450°C will be denoted by CT450, and those with TiO<sub>2</sub> calcined at 850°C will be denoted by CT850.

### Characterizations

The thermal behavior and crystallinity of PVDF-TrFE and its composites were measured with a DSC (Q200, from the TA instruments, USA) at the heating and cooling rates of 10°C min<sup>-1</sup> from room temperature to 200°C under nitrogen atmosphere. The weight of each sample was 5 mg. The first heating and second cooling traces of the samples were recorded.

The X-ray diffraction (XRD) patterns of the membranes were recorded by using a Bruker D8 advanced diffractometer at room temperature. The X-ray source was Ni-filtered Cu K $\alpha$  radiation (voltage 40 kV and current 30 mA). The samples were scanned at a speed of 0.5° min<sup>-1</sup> from 10° to 80°.

Transmission electron microscopy (TEM) was performed to analyze the dispersion of the TiO<sub>2</sub> nanoparticles in the composites by using a Jeol JEM-2010 transmission electron microscope running at 200 kV. The samples were ultra-microtome under cryogenic conditions to a thickness of 60–80 nm.



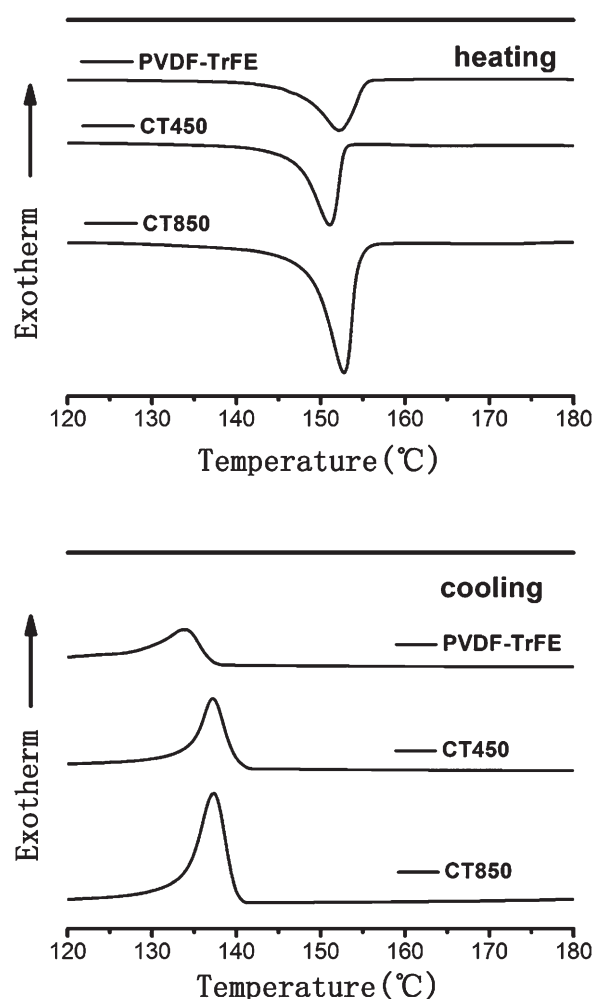
**Figure 1.** XRD patterns of PVDF-TrFE, CT450 (10 wt %), and CT850 (10 wt %).

The dielectric properties of the composites were measured with a 4294A Precision Impedance Analyzer (Agilent) in the frequency range 1000 Hz to 10 MHz at room temperature. Silver electrodes were sputtered on both sides of the composite films (about 10–15-μm thick) for the electrical measurements.

## RESULTS AND DISCUSSION

XRD is a useful method to investigate the evolution of structure for PVDF-TrFE and its composites with TiO<sub>2</sub> nanoparticles calcined at different temperatures. Figure 1 shows the XRD patterns of PVDF-TrFE and PVDF-TrFE/TiO<sub>2</sub> composites with 10 wt % of TiO<sub>2</sub> calcined at different temperatures. In the XRD pattern of PVDF-TrFE, the peak at 20.00° is assigned to the (110, 200) lattice plane, analogous to the characteristic signal of the  $\beta$  ferroelectric phase of PVDF-TrFE.<sup>24</sup> In the XRD pattern of CT450, the peak at 25.35° is assigned to the (1 0 1) lattice plane, analogous to the characteristic peak of anatase TiO<sub>2</sub>; the peak at 20.3° is assigned to the (1 1 0, 2 0 0) lattice plane, analogous to the characteristic peak of the  $\beta$  ferroelectric phase of PVDF-TrFE.<sup>25</sup> In the XRD pattern of CT850, the peak at 27.6° is assigned to the (1 1 0) lattice plane, analogous to the characteristic peak of rutile TiO<sub>2</sub>.<sup>26</sup> The peak at 19.8° is assigned to the (1 1 0, 2 0 0) lattice plane, analogous to the characteristic peak of the  $\beta$  ferroelectric phase of PVDF-TrFE. In both PVDF-TrFE/TiO<sub>2</sub> composites, the characteristic peaks of both PVDF-TrFE and TiO<sub>2</sub> exist, indicating the good dispersion of TiO<sub>2</sub> nanoparticles in the PVDF-TrFE matrix. Besides, no obvious change in the position of the diffraction peaks of PVDF-TrFE in the composites has been found, indicating that the introduction of TiO<sub>2</sub> nanoparticles did not affect the structure of PVDF-TrFE in the composites. It is also been found that the PVDF-TrFE peaks in both composites quickly increased in intensity and became predominant. The increase in intensity suggests increases in crystallinity of PVDF-TrFE in the presence of TiO<sub>2</sub> nanoparticles. The TiO<sub>2</sub> nanoparticles dispersed in the composites play a role in enhancing the crystallization of PVDF-TrFE due to the heterogeneous nucleation effect in the composites.

The crystallization behavior of PVDF-TrFE and PVDF-TrFE/TiO<sub>2</sub> composites with TiO<sub>2</sub> calcined at different temperatures were studied by using differential scanning calorimetry at 10°C min<sup>-1</sup> from 120 to 200°C. The DSC thermograms (the first heating and second cooling traces were recorded) of PVDF-TrFE and PVDF-TrFE/TiO<sub>2</sub> composites with 10 wt % TiO<sub>2</sub> calcined at different temperatures are shown in Figure 2 and the corresponding parameters are summarized in Table I. In the first heating endotherm of PVDF-TrFE, the peak at 152°C, which is lower and broader than the melting peak of PVDF, corresponds to the melting point of PVDF-TrFE ( $T_m$ ).<sup>27</sup> The decrease of  $T_m$  is mainly due to the introduction of TrFE into the PVDF matrix. Furthermore, the  $T_m$  of both composites show no variations compared with PVDF-TrFE, indicating that the TiO<sub>2</sub> nanoparticles in the composites do not affect the melting behavior of PVDF-TrFE. In the cooling cycle, the crystallization temperature ( $T_c$ ) for PVDF-TrFE is 134°C, the value for the PVDF-TrFE/TiO<sub>2</sub> composites with different calcination temperatures of TiO<sub>2</sub> is about 137–138°C (Table I). The higher  $T_c$  of the composites means that the presence of TiO<sub>2</sub> nanoparticles may serve as nucleation centers for PVDF-TrFE and lead to higher crystallization tempera-



**Figure 2.** DSC thermograms of PVDF-TrFE, CT450 (10 wt %), and CT850 (10 wt %).

**Table I.** DSC Parameters of the Pure PVDF, Composite CT450, and Composite CT850

Sample	$\Delta H_m$	$\Delta H_c$	$T_m$	$T_c$	$X_c$ (%)
PVDF-TrFE	14.84	16.45	152.23	133.96	32.97
CT450	19.03	17.33	151.31	137.26	46.98
CT850	28.16	28.73	151.56	138.88	69.53

ture. The same trend can be found in the enthalpy of melting. The composite CT450 exhibits an enthalpy of melting of about 19.03 J g<sup>-1</sup>, and the composite CT850 exhibits an enthalpy of melting of about 28.16 J g<sup>-1</sup>, both higher than the value of about 14.9 J g<sup>-1</sup> for PVDF-TrFE. Higher enthalpy of melting indicates higher extent of crystallinity.

The DSC parameters  $\Delta H_m$ ,  $\Delta H_c$ ,  $T_m$ , and  $T_c$  were summarized in Table I. The degree of crystallinity ( $X_c$ ) of PVDF-TrFE/TiO<sub>2</sub> can be calculated by using the following equation:

$$X_c(\%) = \frac{\Delta H_m}{(1-w)\Delta H_0} \quad (1)$$

where  $\Delta H_m$  is the enthalpy of melting of the sample (J g<sup>-1</sup>),  $\Delta H_0 = 45$  J g<sup>-1</sup> is the enthalpy of fusion for 100% crystalline PVDF-TrFE,<sup>28</sup> and  $w$  is the TiO<sub>2</sub> content in the PVDF-TrFE/TiO<sub>2</sub> composite. The calculated  $X_c$  results are shown in Table I. The  $X_c$  for PVDF-TrFE is 32.97%, and the values for the composites are 46.98% (CT450) and 69.53% (CT850). The increase in  $X_c$  suggests increases in crystallinity of PVDF-TrFE. The TiO<sub>2</sub> nanoparticles accelerated the crystallization of PVDF-TrFE and increased the crystallinity of the composites, in agreement with the XRD results above.

TEM measurements were used to evaluate the dispersion of the TiO<sub>2</sub> nanoparticles in the polymer matrix. Figure 3 shows the TEM photographs of PVDF-TrFE/TiO<sub>2</sub> (10 wt %) composites with TiO<sub>2</sub> calcined at temperature 450 and 850°C. It can be seen that the TiO<sub>2</sub> nanoparticles are separated from each other and dispersed homogeneously in the polymer matrix in both CT450 and CT850. The good dispersion is attributed to the solution cast method with vigorous stirring and ultrasonic treatment and the existence of PVP in the composites. The TiO<sub>2</sub> particle size in the polymer matrix is about 150 nm. There is little agglomeration of the TiO<sub>2</sub> nanoparticles in the matrix because of introduction of high TiO<sub>2</sub> content. From the TEM photographs, we can also see that the addition of TiO<sub>2</sub> nanoparticles does not affect the structure of PVDF-TrFE, in accordance with the XRD results above.

Figure 4 shows the dependence of the dielectric permittivity and dielectric loss tangent ( $\tan \delta$ ) of the PVDF-TrFE/TiO<sub>2</sub> composites CT450 on frequency at room temperature. As shown in Figure 4(a), the permittivity of the PVDF-TrFE/TiO<sub>2</sub> composite decreases as the frequency increases from 1000 Hz to 10 MHz because of the reduction of dipolar contribution at high frequencies.<sup>29,30</sup> Besides, the permittivity increases with increasing content of TiO<sub>2</sub> nanoparticles at constant frequency. For instance, PVDF-TrFE/TiO<sub>2</sub> (30 wt %) has a permittivity of 19

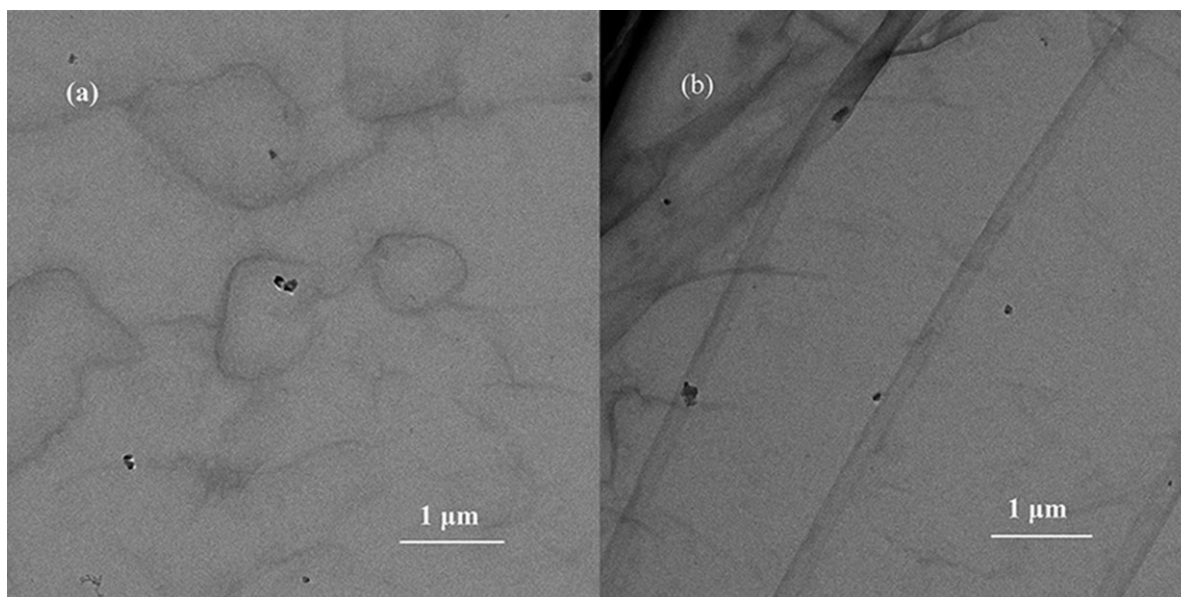


Figure 3. TEM photographs of PVDF-TrFE/TiO<sub>2</sub> (10 wt %) composites with TiO<sub>2</sub> calcined at (a) 450°C and (b) 850°C.

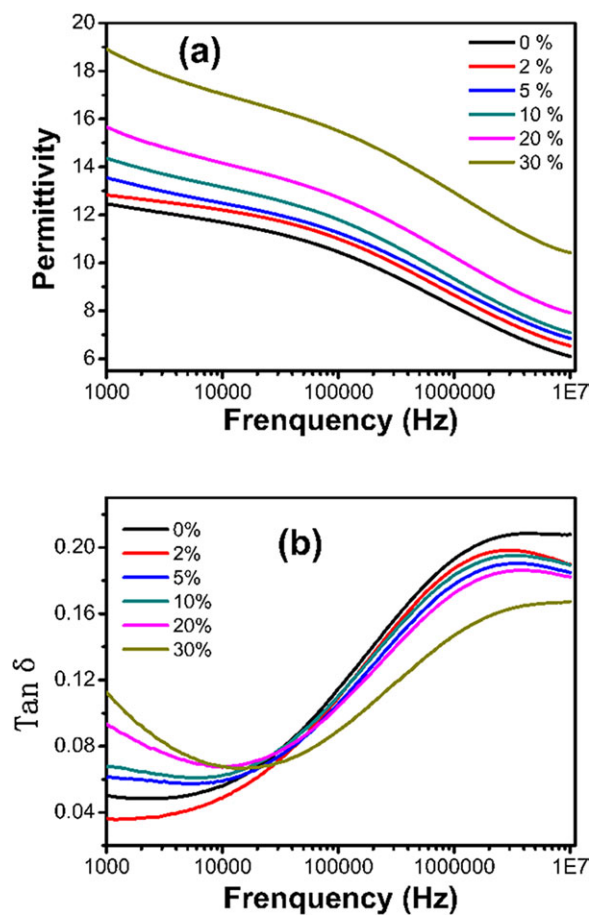


Figure 4. (a) Permittivity and (b) dielectric loss tangent ( $\tan \delta$ ) of PVDF-TrFE and PVDF-TrFE/TiO<sub>2</sub> (CT450) as a function of frequency at different TiO<sub>2</sub> contents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

at 1000 Hz, which is much higher than the value of 12.4 for PVDF-TrFE at 1000 Hz. The increase of permittivity is attributed to the introduction of TiO<sub>2</sub> nanoparticles with higher permittivity into the polymer matrix. As shown in Figure 4(b),  $\tan \delta$  of all the composites increases with the content of TiO<sub>2</sub> at low frequencies because of the increase in interface with the addition of TiO<sub>2</sub> nanoparticles. The large interface leads to Maxwell-Wagner-Sillars (MWS) interfacial polarization at low frequencies and affect the polarization and dielectric responses of the polymer matrix. However, the dielectric loss tangent of the composites at low frequencies is relatively low, indicating that the contribution of the interface is rather low, and  $\tan \delta$  is mainly determined by the polymer matrix.<sup>30,31</sup>

Figure 5 shows the permittivity of the PVDF-TrFE/TiO<sub>2</sub> as a function of TiO<sub>2</sub> content at 1000 Hz and room temperature for

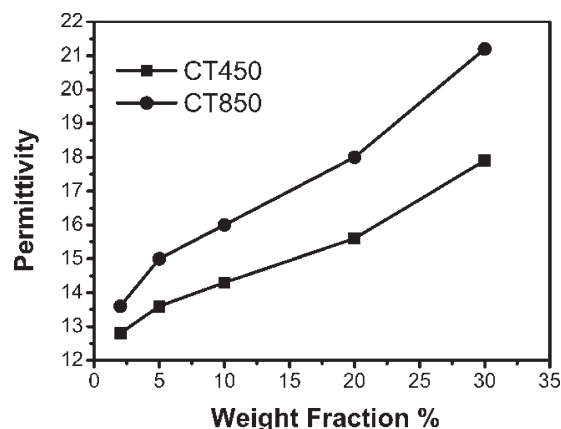


Figure 5. Permittivity of PVDF-TrFE/TiO<sub>2</sub> composites at different TiO<sub>2</sub> contents for TiO<sub>2</sub> nanoparticles calcined at two different temperatures.



TiO<sub>2</sub> calcined at two different temperatures. At a fixed TiO<sub>2</sub> calcination temperature (450 or 850°C), the permittivity of the composite increases with increasing content of TiO<sub>2</sub> nanoparticles, consistent with the results given in Figure 4(a). Besides, the permittivity increases with the increase of calcination temperature at a fixed TiO<sub>2</sub> content. For example, the permittivity at 1000 Hz of the composite CT850 containing 30 wt % TiO<sub>2</sub> is 21.2, much higher than the value of 17.9 for the composite CT450 containing 30 wt % TiO<sub>2</sub> and the value of 12.4 for PVDF-TrFE. There are two reasons for the increased permittivity of the composites over that of PVDF-TrFE. First, TiO<sub>2</sub> nanoparticles have higher permittivity than the pure PVDF-TrFE, as the content of TiO<sub>2</sub> nanoparticles increases, the permittivity of the composites increased. Second, as the calcination temperature of TiO<sub>2</sub> increases, the rutile phase becomes dominant, which has a higher permittivity than the anatase phase. The higher the permittivity of the fillers is, the higher the permittivity of the composites is.

## CONCLUSIONS

Composites of PVDF-TrFE/TiO<sub>2</sub> were prepared by the solution cast method. The crystallization behavior and dielectric properties of the composites with TiO<sub>2</sub> calcined at different temperatures were studied. TEM results showed that the TiO<sub>2</sub> nanoparticles were well dispersed in the polymer matrix and did not affect the structure of the polymer matrix. XRD and DSC measurements showed that the crystallinity of PVDF-TrFE/TiO<sub>2</sub> composites increased as the introduction of TiO<sub>2</sub> with different calcination temperatures. Besides, with the increase in TiO<sub>2</sub> content and the increase in calcination temperature of TiO<sub>2</sub> at constant TiO<sub>2</sub> content, the permittivity of PVDF-TrFE/TiO<sub>2</sub> composite increased rapidly, but the dielectric loss remains at a low level.

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