

Dielectric responses enhanced by nanofiller-polymer interfaces in PVDF-based terpolymer nanocomposites

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Abstract: The interfaces between nanofillers and the polymer matrix in nanocomposites are known to be increasingly important when nanofillers become smaller. A P(VDF-TrFE-CFE) terpolymer is used as the template polymer matrix and low- K (dielectric constant) SiO_2 and high- K BaTiO_3 nanoparticles as fillers to determine the enhancement effect of the interfaces. For both kinds of fillers, anomalous increases in the dielectric constant and polarization response are observed at nanoparticle loading less than 1% (volume fraction). These increases are not related to the intrinsic dielectric properties of the nanofillers and the change of crystallinity of the terpolymer. The crystalline phase is slightly changed from a non-polar structure towards a more polar one, improving the dielectric response in the interfacial regions. An interfacial model is proposed and the non-uniform dielectric response of the interfacial regions is responsible for the observed dielectric phenomena. The overlapping of the interfacial regions leads to the maximum dielectric response of the nanocomposites with certain particle loading.

Key words: dielectric materials; nanocomposites; interfacial effect; terpolymer

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纳米添加物-聚合物界面效应增强 PVDF 基三聚物纳米复合材料的介电响应

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摘要: 在纳米复合材料中, 随着纳米颗粒尺寸的减小, 纳米颗粒与聚合物基体间的界面起着越来越大的作用。为此以 P(VDF-TrFE-CFE) 三元共聚物作为聚合物基体, 以低介电系数的 SiO_2 和高介电系数的 BaTiO_3 纳米颗粒为填料研究了界面的增强效应。对于这两种纳米颗粒, 当体积分数低于 1% 时, 其介电系数和极化响应均出现异常的增加。这些增加与纳米颗粒本身的介电性能及三聚物的结晶度变化无关。聚合物中的结晶相由非极性结构向极性结构有轻微的转变, 因此提高了界面区域的介电响应。对此提出一种界面模型, 解释了界面区域的非均匀介电响应是引起该介电现象的主要原因。在某一纳米颗粒含量下, 界面区域的重叠可带来纳米复合材料最大的介电响应。

关键词: 介电材料; 纳米复合物; 界面效应; 三聚物

0 Introduction

The incorporation of nano-size fillers in polymers to form nanocomposites has been an

important strategy to enhance the properties of polymers, which has been often exploited to improve the mechanical properties of polymers, through utilization of the interfaces between the

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polymer matrix and nanofillers^[1-2]. Nanocomposites have also been utilized to improve the dielectric constant (K) and dielectric strength of polymers^[3-8]. However, the effect of nanofillers on the dielectric properties of polymers is a more complex issue. It is generally accepted that the dielectric properties of composites fall between those of constituent materials. Fillers with high dielectric constant are expected to result in a higher composite dielectric constant. Surprisingly, the addition of nanofillers with lower dielectric constant has been reported to anomalously enhance dielectric properties in some nanocomposites^[9-11]. For example, a significant enhancement of the dielectric polarization of a polyvinylidene fluoride (PVDF)-based terpolymer was observed when a low fraction of ZrO_2 nanoparticles, which have a dielectric constant comparable to that of the terpolymer, was incorporated^[9-10]. This effect was hypothesized to originate from the interfacial regions between the polymer matrix and nanofillers. One of the models about the interfacial regions comprises several layers of different electrical properties and microstructures against the polymer matrix^[11-15]. However, how this type of interface contributes to dielectric responses of nanocomposites requires further study. The understanding of the interfacial role is crucial to the design of high-performance composites with enhanced dielectric properties.

PVDF ferroelectric polymers have been intensively investigated due to the functionalities of these polymers, allowing their use in flexible sensors, actuators, transducers, and energy-related applications. Modification with TrFE (trifluoroethylene) and CFE (chlorofluoroethylene) converts the polymer to relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer with greater dielectric constant (> 40)^[16-18]. PVDF-based polymers are often used under high electric fields, allowing induction of a polarization response with a greater magnitude by electric fields. This in turn gives rise to a better functionality in ferroelectric polymers and pronounced interactions between polymer molecules and incorporated fillers.

In this work, we select the high- K P(VDF-TrFE-CFE) terpolymer as the polymer matrix to study the contribution of the interfacial region. In order to probe the interfacial role, we select nanoparticles with both low- K (SiO_2 nanoparticles) and high- K ($BaTiO_3$ nanoparticles) values relative to the polymer. $BaTiO_3$ has a K value higher than 500 even at a particle size of ~ 85 nm, and the dielectric constant of SiO_2 is ~ 3.9 ^[19-20].

Fillers with K value lower than that of the terpolymer are not supposed to increase the dielectric constant and polarization magnitude of nanocomposites in terms of conventional composite principle. If there is a commonality in dielectric responses that is independent of the K values of the fillers, it must be related with either the polymer matrix or the polymer-filler interface. In addition, the addition of polar functionality on the nanofiller surface is expected to further reveal the effect of the bonding strength between polymers and nanoparticles on dielectric properties.

1 Experimental procedures

P(VDF-TrFE-CFE) (63%/29.7%/7.3% (mole fraction)) was purchased from Piezotech, Arkema. The $BaTiO_3$ (particle size approximately 100 nm) nanoparticle was purchased from Shandong Sinocera Functional Material Co. Ltd. (Shandong, China). The SiO_2 (20 nm) nanoparticle was purchased from XFnano (Nanjing, China). Nanocomposites of P(VDF-TrFE-CFE) with different volume fractions of $BaTiO_3$ and SiO_2 were prepared by a solution cast method. The terpolymer was dissolved in a mixed solvent (90% DMF and 10% MEK). All the nanofillers were dried at 120 °C in a vacuum oven for 5 h to remove the adsorbed water on the surfaces. After that, the nanofillers were dispersed in a mixed solvent (90% DMF and 10% MEK). The mixture was stirred and sonicated in an ultrasound cleaner to obtain a better dispersion of the nanoparticles in the solvent. The terpolymer solution and the nanofiller suspension with different volume fractions were mixed, stirred and sonicated. Finally, the mixture was poured onto a glass slide and dried at 90 °C for 20 min and 70 °C for 2 h. After drying, the terpolymer and nanocomposite film was peeled off from glass slides and placed in a vacuum oven at 110 °C for 5 h to remove the residual solvent and further increase the crystallinity of the terpolymer.

In addition, $BaTiO_3$ nanoparticles were treated by hydrogen peroxide (H_2O_2) to graft more hydroxyl groups onto the particle surface. Typically, 0.2 g $BaTiO_3$ nanoparticles were added into 80 ml H_2O_2 aqueous solution and stirred at 90 °C for different durations. Then, the particles were filtered and washed with de-ionized water. Finally, the modified nanoparticles were dried at 105 °C for 5 h to remove the water. To determine the amount of hydroxyl groups on the surface of $BaTiO_3$ nanoparticles after H_2O_2 treatment for different times, the treated nanoparticles were

dried for the same duration and then exposed in the air to absorb water for 50 h. The amount of hydroxyl groups was measured by the weight loss of treated particles using a thermogravimetric analysis (TGA, Q5000IR, TA Instruments, USA).

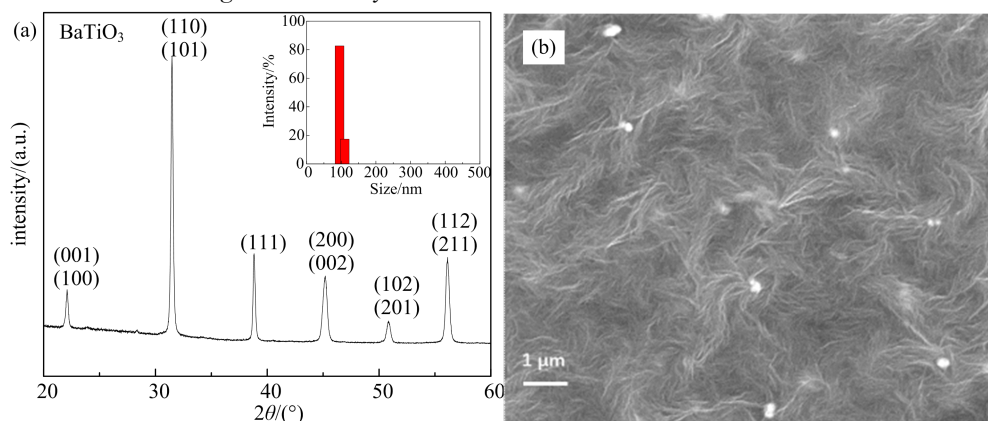
For dielectric measurement, gold electrodes were deposited on the surface of the terpolymer and its nanocomposites using a DC sputter coater (EMS150T, Electron Microscopy Sciences, Hatfield, PA, USA). The polarization-electric field (P-E) hysteresis loops were measured using a modified Sawyer Tower circuit (Polyktech, State College, USA). The dielectric breakdown field of the film samples was measured using a breakdown test circuit (Polyktech, State College, USA) and a high-voltage amplifier (Trek 610E, Trek, USA). The weak-field complex dielectric responses were measured using a setup composed of an E4980 LCR meter (Agilent Technology, Santa Clara, CA, USA) and a furnace. The X-ray diffraction (XRD) data of the composites were obtained on a Rigaku Smartlab diffractometer (Rigaku, Tokyo, Japan). The FTIR (Fourier transform infrared spectroscopy)-ATR (attenuated total reflectance) of the samples was obtained with Nicolet 6700 (Nicolet, Madison, WI, USA). The microstructure of the composites was observed on a scanning electron microscope (SEM, SU8220, HITACHI, Japan). Differential scanning calorimetry (DSC,

TA Q2000, TA Instruments, USA) was used to obtain crystallinity, the melting temperature, and crystallization temperature of the terpolymer and nanocomposites.

2 Results and discussion

2.1 Analysis of microstructure in nanocomposites

Fig. 1(a) shows the XRD pattern of BaTiO₃ nanoparticles, revealing a perovskite structure. The particle size was determined to be ~100 nm by the dynamic light scattering method, as shown in the inset of Fig. 1(a). These particles are big enough to exhibit high polarity and a dielectric constant much greater than 500, which can increase both the dielectric constant and the polarization of the terpolymer composite. These particles are typically added in a large amount to generate a nanodielectric composite with a high dielectric constant; however, the addition of this large amount can also result in lower mechanical and dielectric strength. In this study, we purposely kept the filler loading minimal to avoid these issues. Fig. 1(b) shows the dispersion of BaTiO₃ particles in the terpolymer matrix. The BaTiO₃ nanoparticles appear as white dots and are relatively well-dispersed in the terpolymer matrix. No major agglomerates greater than 200 nm in size are observed.



(a) The XRD patterns of BaTiO₃ particles. The inset shows the size distribution of BaTiO₃ nanoparticles in the DMF solvent detected by dynamic light scattering technique. (b) The SEM image of nanocomposite containing 0.8% (volume fraction) BaTiO₃ nanoparticles.

Fig. 1 The microstructure, particle size of the BaTiO₃ nanoparticles, and their dispersion in the terpolymer

As a semicrystalline polymer, the terpolymer exhibits strong dielectric properties largely from its crystalline phase. Higher crystallinity is favorable for the dielectric properties. In order to determine the influence of added BaTiO₃ nanoparticles on the crystallinity and the thermal stability of the terpolymer, DSC measurements were taken near the melting temperature, as shown in Fig. 2. The analysis of these curves provided the melting

temperature and melting heat data for the terpolymer and the nanocomposites, as summarized in Tab. 1. It is seen that the addition of nanoparticles does not change the melting heat and the melting temperatures of the terpolymer significantly.

Fig. 3(a) shows the XRD patterns of the terpolymer and nanocomposites prepared with different BaTiO₃ concentrations. The crystalline

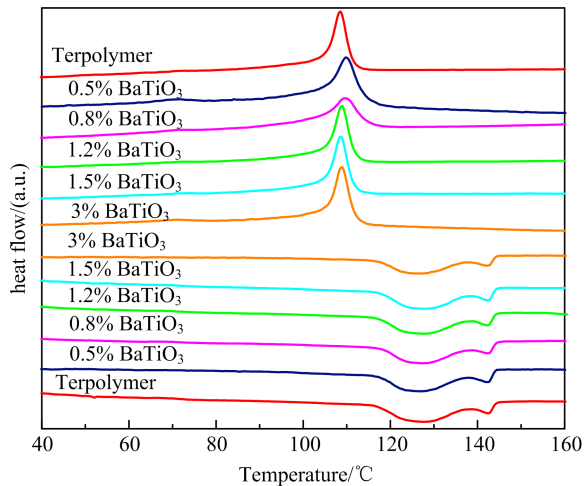


Fig. 2 DSC curves of nanocomposites with various BaTiO₃ particle loadings (volume fraction)

Tab. 1 The melting peak temperature, melting enthalpy and crystallization temperature of nanocomposites with various BaTiO₃ particle loadings (volume fraction)

Compositions	Melting peak temperature/°C	Melting enthalpy / (J · g ⁻¹)	Crystallization temperature/°C
Terpolymer	128.50	17.30	108.56
0.5% BaTiO ₃	127.75	16.91	109.71
0.8% BaTiO ₃	128.46	17.09	109.54
1.2% BaTiO ₃	128.13	17.64	108.94
1.5% BaTiO ₃	128.70	17.57	108.70
3% BaTiO ₃	127.85	14.41	108.95

phase of P(VDF-TrFE-CFE) terpolymer has a α -like structure and in the composites, the terpolymer matrix remains in an α -like crystal structure, with no significant changes in the crystal structures as determined by the XRD patterns^[21].

The FTIR analysis was further performed to investigate the effect of nanofillers on the microstructure of the nanocomposites, and the FTIR spectra of the composites with different compositions are shown in Fig. 3(b). To probe the possible slight change of the microstructure of nanocomposites, the normalized intensity of the FTIR spectra was shown in the figure, which was calculated by

$$I_n = (I - I_{\min}) / (I_{\max} - I_{\min}) \quad (1)$$

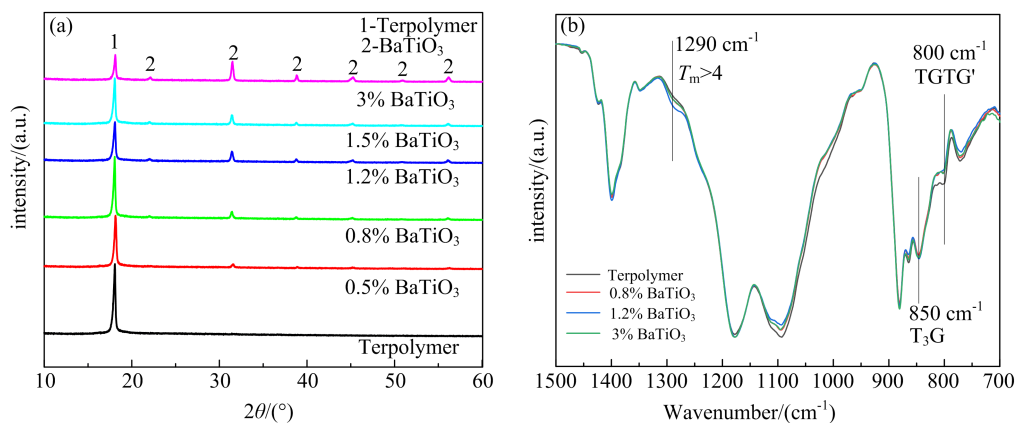
where I , I_{\min} , and I_{\max} are the measured intensity, the minimum intensity, and the maximum intensity from the FTIR spectrum of a material. As revealed by the spectra, the terpolymer exhibits a microstructure close to the α -like phase, and the peak at 1290 cm⁻¹, which is assigned to $T_m > 4$ conformation, is weak^[22]. The addition of nanofillers slightly changes the microstructure of

the terpolymer and the peak intensity at 1290 cm⁻¹ increases with particle loading. Accordingly, the peak at approximately 800 cm⁻¹, which is related to the TGTG' conformation, slightly decreases with the addition of nanoparticles. The peak at approximately 850 cm⁻¹, which is assigned to T₃G conformation, almost does not change in the composites. The FTIR results suggest that the addition of BaTiO₃ can induce more polar phases from the originally non-polar α -like phase in the terpolymer. Since the particle loading of composites is low, the structure change of the terpolymer is believed to occur at interfacial regions between the terpolymer and nanoparticles.

2.2 Weak-field dielectric responses

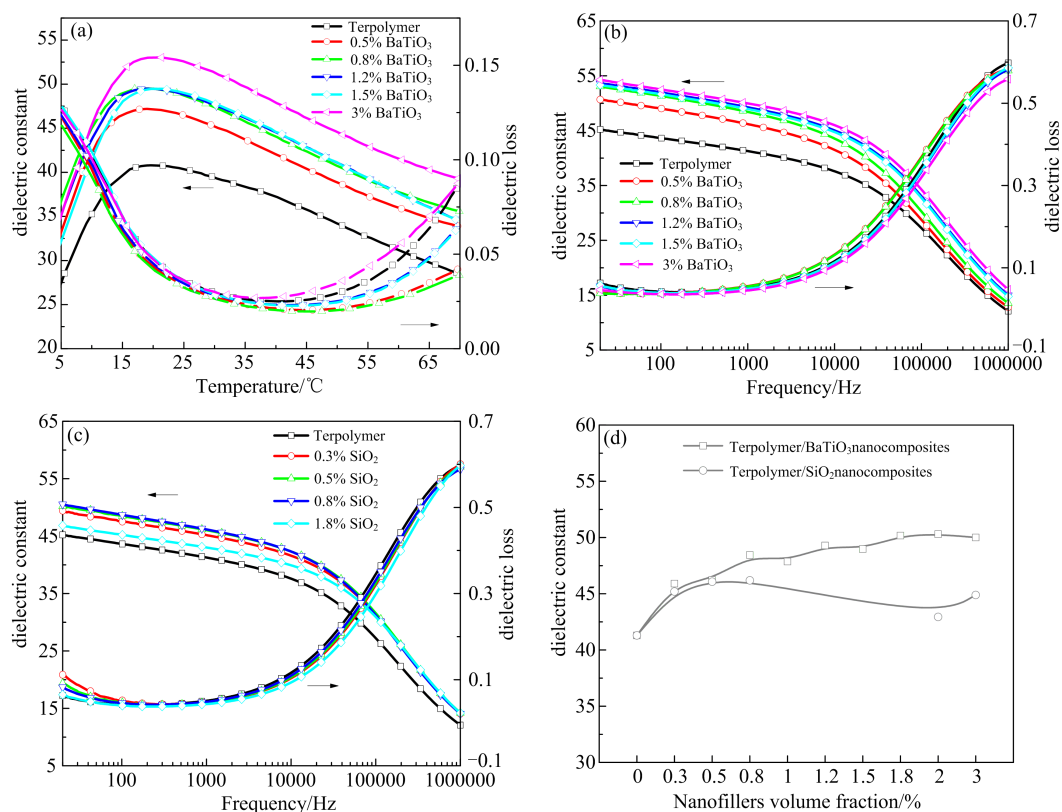
The weak-field dielectric responses of the terpolymer and nanocomposites as a function of temperature were determined as shown in Fig. 4 (a). The P(VDF-TrFE-CFE) terpolymer is a typical relaxor ferroelectric material, which exhibits a broad dielectric peak at around 20°C. The addition of BaTiO₃ nanoparticles did not significantly change the temperature-dependent dielectric behavior of the terpolymer, but there was an increase in the dielectric constant across the entire temperature range. At low temperatures, the dielectric loss of the nanocomposites was similar to that of the terpolymer. At above 40°C, the dielectric loss of the nanocomposites was even lower than that of the terpolymer for BaTiO₃ concentrations below 1.5% (volume fraction). The frequency dependence of the dielectric properties of both terpolymer and nanocomposites at room temperature was determined and are also shown in Fig. 4(b). From 20 Hz to 1 MHz, the dielectric constant of the composites was higher than that of the terpolymer control. The dielectric loss of the nanocomposites was almost the same as that of the terpolymer. The effect of the small amount of nanofiller on the dielectric constant of the terpolymer was replotted as shown in Fig. 4(d). The introduction of nanoparticles caused two types of dielectric enhancement: a rapid increase in the dielectric constant from ~ 40 to ~ 49 at concentrations below 1% (volume fraction) BaTiO₃, and a slow increase to ~ 50 above 1% (volume fraction) BaTiO₃.

BaTiO₃ is a typical ferroelectric material with a high dielectric constant and a high spontaneous polarization. BaTiO₃ particles of 100 nm in diameter should have a dielectric constant much higher than 40 of the terpolymer. One may think that the enhancement of the dielectric constant in the nanocomposites is a normal phenomenon



(a) The XRD patterns. (b) The FTIR spectra.

Fig. 3 The microstructure of the terpolymer and the nanocomposites with different BaTiO₃ particle loadings (volume fraction)



(a) The temperature dependence of the dielectric responses for the terpolymer/BaTiO₃ nanocomposites at 1 kHz. (b) The frequency dependence of the dielectric responses at room temperature for the terpolymer/BaTiO₃ nanocomposites. (c) The frequency dependence of the dielectric responses at room temperature for the terpolymer/SiO₂ nanocomposites. (d) The variation of weak-field dielectric constant of the terpolymer nanocomposites with the concentration of BaTiO₃ and SiO₂.

Fig. 4 The weak-field dielectric responses of P(VDF-TrFE-CFE) terpolymer, terpolymer/BaTiO₃ nanocomposites, and terpolymer/SiO₂ nanocomposites with different particle loadings (volume fraction)

associated with the addition of BaTiO₃ nanofillers. The subsequent experimental results in terpolymer composites containing low-*K* SiO₂ nanoparticles do not support this assumption. By adding SiO₂ (dielectric constant $K \sim 3.9$), the dielectric constant should be reduced because of the addition principle. However, a similar increase in dielectric constant was also observed for terpolymer contained a similarly low fraction of SiO₂

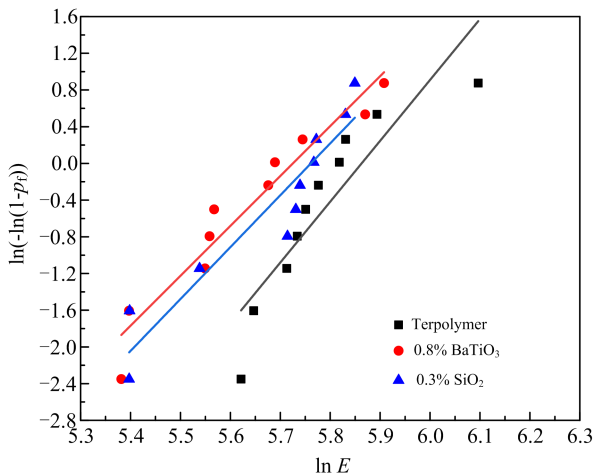
nanoparticles. Fig. 4 (c) shows the weak-field dielectric properties of the terpolymer/SiO₂ nanocomposites with different amounts of particles. The dielectric constant of the terpolymer/SiO₂ composites was obviously enhanced after the addition of SiO₂ at levels below 1.8% (volume fraction), as shown in Fig. 4 (d). This comparative study reveals an unusual but common phenomenon in low-filled terpolymer

composites that is independent of the K values of nanofillers. Therefore, this commonality in the dielectric constant enhancement should have a close relationship with the interfaces between nanoparticles and the polymer matrix.

It should be pointed out that in this work, the study is mainly focused on the terpolymer/BaTiO₃ composites and the terpolymer/SiO₂ composites are investigated to show the effect of dielectric properties of the nanofillers on those of composites. There are many studies regarding nanocomposites filled by SiO₂, and except dielectric properties, we will not provide structural investigation in this work^[23-30].

2.3 High-field polarization responses

The effect of nanofillers on the dielectric terpolymer was next investigated under high electric fields. To avoid the complications due to breakdown damages in the samples when testing under high electric fields, the DC dielectric breakdown voltage was measured prior to the polarization tests. The results for the terpolymer, terpolymer/BaTiO₃ (volume fraction 0.8%) nanocomposites, and terpolymer/SiO₂ (volume fraction 0.3%) nanocomposites are presented as Weibull distributions, as shown in Fig. 5. The characteristic breakdown strength was determined as 344 MV/m for the terpolymer, 299 MV/m for the terpolymer/BaTiO₃ composite, and 310 MV/m for the terpolymer/SiO₂ composite.



p_f is the cumulative failure, and E is the breakdown electric field of the tested samples.

Fig. 5 The Weibull analysis of the breakdown strength of the P(VDF-TrFE-CFE) terpolymer, the nanocomposites containing 0.8% (volume fraction) BaTiO₃, and the nanocomposites containing 0.3% (volume fraction) SiO₂

In the polarization switching tests, an electric field of 200 MV/m was used to ensure that the material was far from the breakdown limit. Fig. 6

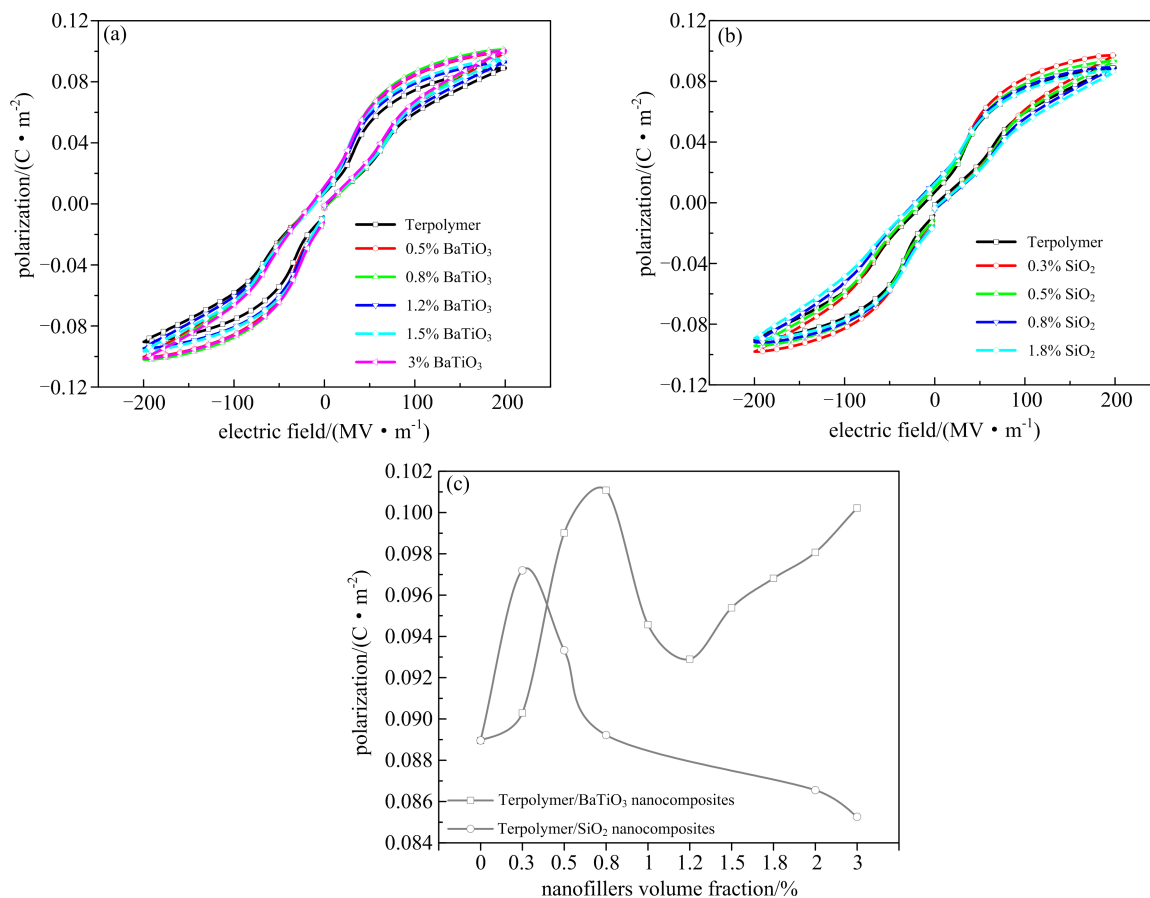
(a) shows the P-E hysteresis loop of the terpolymer and the BaTiO₃-containing composites. An inspection on the P-E loops reveals a subtle composition dependence of the high-field polarization response. Re-plotting the dependence indicates that the nanocomposites possess a greater polarization response than the control sample, as shown in Fig. 6(c). Different than the weak-field dielectric response, the induced polarization peaks at a BaTiO₃ loading of 0.8% (volume fraction). After a reduction at 1.2% (volume fraction), the polarization then increased continuously with increasing BaTiO₃ loading.

The similar effect of the low- K SiO₂ nanoparticle on the high-field polarization was also observed, as shown in Fig. 6(b) and Fig. 6(c). The dipolar hysteresis loop (Fig. 6(b)) exhibits a similar change with increased SiO₂ loading. The maximum polarization was observed in a composite containing 0.3% (volume fraction) SiO₂ (Fig. 6(c)). Different from the behavior of the BaTiO₃ nanocomposites, SiO₂ composites exhibit decreasing polarization values after reaching the maxima. The polarization further decreases with increasing SiO₂ loading, becoming lower than that of the terpolymer at amounts above >1% (volume fraction).

The results in Fig. 6 suggest that the enhanced polarization response in both nanocomposites with nanofillers lower than 1% (volume fraction) may be dominated by the same mechanism regardless of K values of the nanofillers. Moreover, this is more associated with the interfacial response to the applied electric field in both cases. The anomalous phenomenon dominates the dielectric responses of the composites only at low amounts of nanofillers (0.8% (volume fraction) for terpolymer/BaTiO₃ composites and 0.3% (volume fraction) for terpolymer/SiO₂ composites). The lower threshold for terpolymer/SiO₂ may reflect the stronger contribution of smaller particle size of SiO₂ (~20 nm).

2.4 Effect of enhanced filler-polymer interfaces

In order to better understand the dominant mechanism of the filler-polymer interface on the dielectric properties, we next added highly polar functionality by grafting the nanofiller surface with hydroxyl groups. This added functionality should generate a stronger interaction between the polar fillers and polar polymer, and thus further constrain the interfacial dipoles. Changing the amount of the hydroxyl groups on the surface of BaTiO₃ nanoparticles should significantly change the strength of bonding between the terpolymer



(a) P-E loop for terpolymer/BaTiO₃ at room temperature; (b) P-E loops for terpolymer/SiO₂ all measured at 10 Hz and 200 MV·m⁻¹; (c) The variation of polarization response with the concentration of BaTiO₃ and SiO₂ under 200 MV·m⁻¹.

Fig. 6 The polarization responses of terpolymer composites with BaTiO₃ and SiO₂ nanoparticles of different loading fractions(volume fraction)

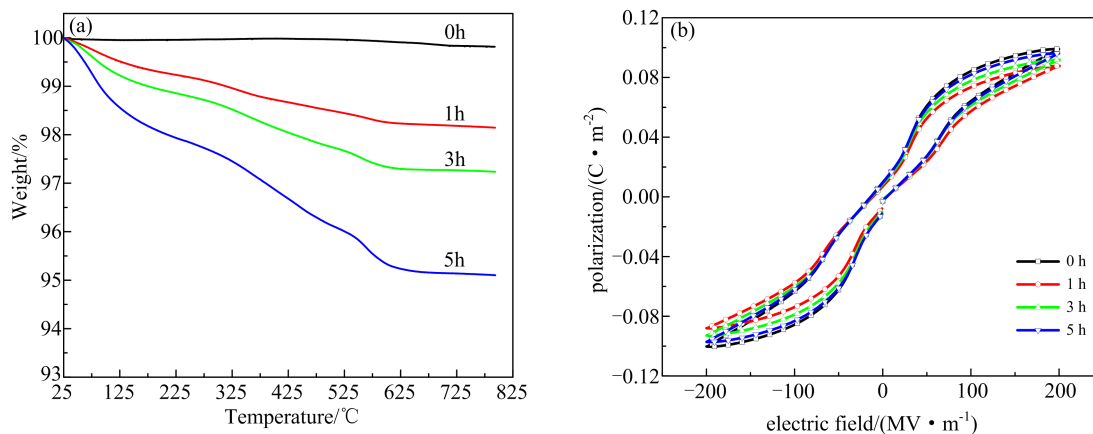


Fig. 7 (a) TGA plot of BaTiO₃ particles treated in H₂O₂ for different durations.

(b) Dipolar P-E loops of the nanocomposites with 0.5% (volume fraction) BaTiO₃ tested at 10 Hz.

and nanoparticles. To prepare these materials to test this hypothesis, BaTiO₃ nanoparticles were treated in H₂O₂ for different amounts of time to achieve different quantities of hydroxyl groups. The treated particles were then exposed in the air for 50 h. Because the hydroxyl groups have a strong affinity with water, the amount of adsorbed water can be used as an indicator of the amount of hydroxyl groups on the surface of the BaTiO₃.

Fig. 7 (a) shows the TG analysis of the H₂O₂-treated BaTiO₃ nanoparticles. The early weight loss between 100°C and 200°C can be attributed to the dissociation of the adsorbed water, and the loss at higher temperatures is associated with the removal of the hydroxyl groups^[31]. The results indicated that the increased length of H₂O₂ treatment resulted in increased density of the hydroxyl groups on the surface of BaTiO₃

nanoparticles.

The polarization response was next tested for these samples with different amounts of hydroxyl groups, using the same P-E test protocol as that used for the non-modified materials. Fig. 7 (b) shows the P-E loops of the nanocomposites containing 0.5% (volume fraction) BaTiO₃ nanoparticles with and without H₂O₂-treatment. Overall, the H₂O₂ treatment on BaTiO₃ nanoparticles reduced the polarization response of the nanocomposites, and this was true for samples modified for different lengths of time. This result suggests that the interfacial interaction between the terpolymer matrix and nanoparticles indeed plays an important role in the polarization response. For the nanoparticles with more hydroxyl groups (longer treatment), the interaction between polymer molecules and nanoparticles was stronger, which limited the mobility of orientation of the interfacial dipoles and thus lowering the polarization enhancement. For nanoparticles treated for 3 h or longer, the extra hydroxyl groups may also respond to the electric field in addition to the interfacial dipoles, which will alter the total polarization response of the composites.

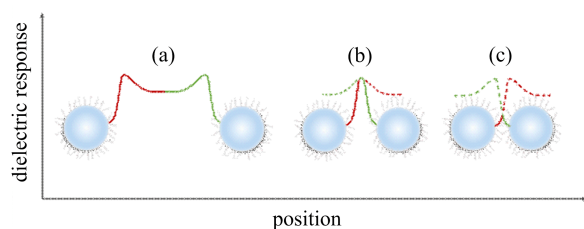
Conventionally, in order to enhance the dielectric properties of polymers, a high volume of inorganic nanofillers with high dielectric properties are added to the polymers. Although the dielectric properties of polymers can be improved by this composite approach, some adverse effects may be produced. The flexibility of polymers becomes deteriorated by adding a large amount of nanofiller. Furthermore, for some high-electric-field applications, the dielectric breakdown field of nanocomposites can be significantly reduced owing to the concentration of electric fields in the polymer phase with a low dielectric constant and the generation of a large amount of defects after the addition of nanofillers. However, there are a few (though rare) reports showing that the addition of a smaller amount of nanofiller can significantly improve the dielectric response of nanocomposites, even that the dielectric constant of the nanofillers is comparable to that of polymer matrix^[9,10,11,32]. Because only a small amount of nanoparticle is added, the flexibility and breakdown field of the composites will not be much affected, as also observed in this work. This enhancement effect is anomalous because the dielectric response of the nanocomposites is much higher than that predicted by any existing dielectric model for diphasic composites, which may raise

the suspicion whether this effect is real. In our work, the similar dielectric enhancement effect was observed in PVDF terpolymer/BaTiO₃ and PVDF terpolymer/SiO₂ nanocomposites with a small amount of nanoparticle, confirming that this anomalous phenomenon is real. Furthermore, nanoparticles with dielectric constant much higher (BaTiO₃, $K \sim 1000$) or much lower (SiO₂, $K \sim 3.9$) than that of PVDF terpolymer ($K > 40$) were intentionally selected as the fillers of the composites. Both nanocomposites exhibit greatly enhanced weak-field and high-field dielectric response (Fig. 4 and Fig. 6) regardless of the dielectric properties of the nanofillers. These results suggest that the enhancement at very low nanoparticle loading is a general phenomenon in nanocomposites and is not related to the dielectric properties of nanofillers. However, the magnitude of the enhancement can be affected by different factors, such as the size and the surface chemistry of particles.

Because only a small amount of nanoparticle was added, except in the interfacial regions, the dielectric properties of the majority portion of the polymer matrix should not be significantly modified. The interfacial regions should cause a much higher dielectric response than the other part of the polymer matrix. At present, the microscopic mechanisms for the anomalously large dielectric constant in the interfacial regions remain obscure and our work may shed some light on the origin of the interfacial effect. For PVDF-based semicrystalline polymers, their dielectric response mainly originates from the crystalline phase. As shown in the XRD patterns in Fig. 1(a), the crystal structure of the polymer matrix almost shows no change with the addition of the nanoparticles. However, a more subtle study by FTIR shown in Fig. 3(b) suggests a slight change of chain conformation from TGTG' to $T_m > 4$ by the addition of the nanoparticles. The change should mainly occur in the interfacial region. For P(VDF-TrFE-CFE) terpolymers, the incorporation of several percent of bulky CFE causes the transformation of the crystalline phase from polar β -phase (mainly $T_m > 4$ conformation), to non-polar α -like structure (largely TGTG' conformation). The excellent properties of the terpolymers, such as high dielectric response and large field induced strain, are associated with the transition from non-polar phase to polar phase, which can be induced by applied electric fields^[33]. The FTIR study of the nanocomposites reveals that the addition of particles can also induce the

similar transition from TGTG' conformation to $T_m > 4$ conformation, which should primarily occur in the interfacial regions. It implies that the energy barrier for the phase transformation in the interfacial regions is reduced in the nanocomposites under an electric field, and this is believed to be one important working mechanism for the enhancement of the dielectric properties. Another possible factor affecting the dielectric properties of the terpolymers is crystallinity of the terpolymer. The DSC results (Tab. 1) indicate that the crystallinity is close to or even lower than that of terpolymer and the change of crystallinity should not be responsible for the enhanced dielectric properties.

In addition, this work also reveals the importance of surface chemistry for the enhancement of dielectric properties. The existence of hydroxyl groups on the particle surface is helpful for the dispersion of nanoparticles in the polar solvent and the polymer matrix. However, more hydroxyl groups may also result in a stronger bonding between the polymer and nanoparticles, which constrains polymer chains. This may increase the energy barrier for the phase transition. Consequently, a higher concentration of hydroxyl groups weakens the dielectric enhancement effect of the nanocomposite, as shown in Fig. 7.



(a) low loading, (b) medium loading, (c) high loading.

Fig. 8 The schematic model of the dielectric response of nanocomposites with different particle loadings

Although interfacial regions have a higher dielectric response than the majority portion of the polymer matrix, their dielectric responses could be spatially non-uniform. Because the hydroxyl group enhances the bonding to the polymer, generating a constraint to the polymer chain, polymer chains adjacent to the particle surface should have a lower dielectric response than those far away from the surface. It can be expected that the dielectric response of interfacial regions increases from the surface, reaches a maximum value, and then drops to the original dielectric response of the polymer. This argument is consistent with the multilayer interfacial model for nanocomposites^[11-12]. The non-uniform distribution of the dielectric response of

the polymer between two particles is schematically shown in Fig. 8(a). In the figure, the two particles are too far away from each other to have the direct interaction of interfacial regions. Compared with the neat polymer, the dielectric response of the nanocomposites is enhanced due to high dielectric response of the interfacial regions. By increasing the particle loading, the interfacial distance reduces, which may lead to the overlapping of the interfacial regions and further increase of the dielectric response. As a result, the overall dielectric response of the composites varies with the change of interparticle distance. The highest dielectric response is reached when the interfacial regions of the two nearest particles meet at the position with the maximum dielectric response, as schematically shown in Fig. 8 (b). When the interparticle distance is further reduced with increasing particle loading, the interfacial regions seriously overlap at the position exhibiting a lower dielectric response, and the dielectric response of polymer matrix is then reduced as shown in Fig. 8 (c). When the concentration of the nanoparticles is further increased, the dielectric properties of nanoparticles will become a dominant factor affecting the properties of composites. This simple schematic model explains the anomalously enhanced dielectric properties observed in the nanocomposites with very low particle loading and the also the observation of the maximum dielectric response of nanocomposites with slightly higher particle loading. From Fig. 4(d) and Fig. 6(c), we can see that the weak-field dielectric response and the high-field polarization response exhibit different composition dependent behaviors. This may be caused by the fact that the terpolymer is a non-linear dielectric material and its dielectric response is strongly dependent on the applied electric field.

Our results have important implication for the design of dielectric materials with improved functionalities. The dielectric properties, especially high field polarization response, are closely related to some important functional properties of polymers, such as the energy storage density and the electric-field induced strain^[9,16,18]. Our study suggests that the addition of a small amount of nanonanoparticle (typically less than 1% (volume fraction)) could significantly improve the dielectric properties. At such low particle loading, other important physical properties for practical applications, such as the mechanical flexibility and dielectric breakdown field, are not compromised. Also, we show that the enhancement effect is

unrelated to the dielectric properties of nanoparticle although the size of the particle is indeed an important parameter. Therefore, we can select cheap nanofillers to achieve low-cost nanocomposites with improved dielectric properties.

3 Conclusions

The dielectric properties of the P(VDF-TrFE-CFE) terpolymer-based nanocomposites were investigated using weak field and high field dielectric techniques. The dielectric constant under weak field and the polarization response under high electric fields were anomalously enhanced in the terpolymer containing a small amount of BaTiO₃ or SiO₂ nanoparticles. This enhancement is attributed to the existence of the interfacial regions with a higher dielectric response than the neat polymer. An interfacial model was postulated as a working mechanism for the anomalous enhancement of dielectric constant and polarization at lower nanofiller concentrations. In the interfacial regions, the enhanced dielectric response of the terpolymer by the addition of nanoparticles is caused by the transformation from a non-polar crystalline phase to a structure with more polar chain conformation, leading to a reduced energy barrier for the dielectric response upon the application of the electric field. Furthermore, the dielectric response of the polymer in the interfacial regions is nonuniform. The bonding between the surface of particles and the polymer may constrain the polymer chain, leading to a low dielectric response. The dielectric response of polymers in interfacial regions varies with the distance from particles and exhibits a maximum value at a certain distance. When the interparticle distance is reduced with increasing the particle loading, the largest dielectric enhancement of the nanocomposites occurs because the interfacial region of the nearest particles overlaps at the position where the highest dielectric response is reached. We also show that treating the nanofillers with hydroxyl groups using H₂O₂ can manipulate the filler-polymer bonding strength and the interfacial dipoles in the nanocomposites for a desirable polarization enhancement. This type of study is important for the understanding of the anomalous interfacial effect in nanodielectrics.

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