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Enhanced Energy Storage Characteristics in PVDF-Based Nanodielectrics With Core-Shell Structured and Optimized Shape Fillers

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ABSTRACT Introducing high-permittivity nano-fillers into a dielectric polymer is a practical way to enhance the permittivity of nanocomposite dielectrics. However, this normally leads to a decrease in the breakdown strength, which has limited the development of electrostatic capacitors. In this work, silica (SiO₂) coating and polydopamine (PDA) surface modification methods were combined for enhancement of the breakdown strength; we prepared poly(vinylidene fluoride) (PVDF) based composite dielectrics doped using double core-shell structure BaTiO₃ nano-particles (BT NPs) and nano-fibers (NFs) (PDA-SiO₂@BT NPs/PVDF or PDA-SiO₂@BT NFs/PVDF). Then, the contributions of the double-layer core-shell structure and filler shape to improving the energy storage performance of the dielectrics were systematically discussed. The results show that the synergy between the silica and PDA effectively increased the breakdown strength. Furthermore, the dielectric properties and energy storage properties of the PVDF-based dielectrics with various double core-shell filler (PDA-SiO₂@BT NPs or PDA-SiO₂@BT NFs) contents were also investigated. Compared with the particles, appropriate introduction of the PDA-SiO₂@BT NFs could more preferentially improve the energy storage characteristics. It was found that 1.0 vol.% PDA-SiO₂@BT NFs/PVDF exhibited a high energy storage density of 14.7 J/cm³ with an efficiency of 68%. This research provides a promising avenue for enhancing the energy storage capability of PVDF-based nanocomposite dielectrics.

INDEX TERMS Nanofiber, core-shell structure, polydopamine, silica, poly(vinylidene fluoride), energy storage density.

I. INTRODUCTION

Dielectric capacitors have been extensively used in electronic devices and power grids for energy storage because of their high power density [1]–[4]. However, the mediocre energy density (U_e) of commercially available electrostatic capacitors, such as biaxially oriented polypropylene (BOPP), is not sufficient to for the continued improvement of energy storage devices [4]–[6]. Consequently, improving the energy storage density of the dielectric is crucial. For dielectric capacitors,

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the energy storage density (U_e) can be calculated by:

$$U_e = \int E dD, \quad (1)$$

where E and D are the applied electric field and displacement, respectively [2]. Specifically, for linear dielectrics:

$$U_e = 0.5\varepsilon_0\varepsilon_r E_b^2, \quad (2)$$

where ε_0 , ε_r , and E_b are the vacuum permittivity, relative permittivity of the dielectric, and the breakdown strength, respectively [3]. Ferroelectric ceramics have a higher relative permittivity and a lower breakdown strength, while polymers have a lower relative permittivity and a higher breakdown

strength [4]. These two types of energy-storage dielectric materials can complement each other. Hence, in recent years, the method of introducing high-permittivity ceramic fillers into a processable polymer such as PVDF has been extensively studied [7]–[9]. A large amount of doping not only leads to increased permittivity but also a decrease in the breakdown strength [10]. There are three reasons for this decline. 1) Because of the large difference in permittivity between matrix and filler, electric field distortion occurs at the interface. 2) The large surface energy of the inorganic particles can cause agglomeration. This results in defects such as voids caused by poor organic and inorganic compatibility. 3) The breakdown strength of the ceramic filler is low. Therefore, a large amount of doping makes the composite dielectric more prone to breakdown. However, if the doping amount is too low, there may not be an enhancement of the dielectric constant. This inherent inverse relationship between the permittivity and the breakdown strength poses restrictions on the achievable performance [7]. Therefore, a comprehensive consideration of the influence of the various parameters on the energy storage dielectric is still an open issue, and such work is needed to improve the energy storage characteristics of the dielectric.

Researchers have made significant efforts to simultaneously improve both ϵ_r and E_b , and some valuable made progress has been made [7], [11], [12]. The method of placing a low dielectric constant and highly insulating buffer layer (such as silicon dioxide, titanium oxide, or aluminum oxide) at the interface between the filler and the substrate is a very effective one [13]–[19]. Wang *et al.* demonstrated that coating SiO₂ layers on the surface nano-particles significantly reduces the energy loss of the nanocomposites under high applied electric fields [14]. Qiu *et al.* reported that the TiO₂@MWCNTs/PVDF composites presented enhanced breakdown strength, permittivity, and a lower dielectric loss compared with pristine MWCNTs/PVDF composites [15]. Lin *et al.* prepared a titanium dioxide-encapsulated barium titanate nanofiber-doped PVDF-based composites and found that the electrical displacement increased while the breakdown strength was well maintained [16]. Surface modification can reduce the difference in surface energy between the materials and improve compatibility of the filler with the matrix. Ye *et al.* used PDA to encapsulate barium titanate particles via the condensation reaction, and they improved the compatibility of the polymer nanocomposite and further improved the breakdown strength [17]. Hu *et al.* made a series of PVDF-based composites doped with modified BT and found that the energy storage density greatly increased [18], [19]. In addition to surface modification, the effects of the filler shape has also been extensively studied. For instance, Sodano *et al.* prepared one-dimensional fillers and found that fiber-filled composite dielectric had better breakdown, dielectric, and energy storage characteristics [20]. That is to say, changing the shape of the filler is also a very effective method to improve the energy storage characteristics of composite dielectrics. Nevertheless, there is still a lack of

systematic consideration and design using the various influencing parameters. Therefore, in this paper, the above two methods were integrated and various energy storage parameters (including the permittivity, breakdown strength, and energy storage efficiency) were considered with the goal of improving the energy storage characteristics of the composite dielectrics.

First, the breakdown strengths before and after SiO₂ coating of the BT-doped PVDF composite dielectrics were compared. It was found that coating SiO₂ on the fillers resulted in a marked effect on the breakdown strengths. Further, PDA was used to modify the surface of the filler to further improve the breakdown strength. Next, the doping content and shape were considered for optimal performance. By comparison, it was found that a small amount of doped fibrous filler was beneficial for enhancing both the permittivity and the energy storage characteristics. The 1 vol.% PDA-SiO₂@BT NFs/PVDF sample displayed the best energy storage characteristics (energy storage density of 14.7 J/cm³ and energy storage efficiency of 69%). This work can serve as a reference for comprehensively improving the energy storage characteristics of composite dielectrics.

II. EXPERIMENTAL

A. MATERIALS AND METHODS

1) MATERIALS

The raw materials used in this work were as follows: PVDF(FR 401) was provided by Shanghai 3F New Material Co., Ltd., China; Polyvinylpyrrolidone (BT NPs (60 nm)) was provided by Shandong Sinocera Functional Material Co., Ltd., China; Tetrabutyltitanate (Ti(OCH₂CH₂CH₂CH₃)₄), barium hydroxide (Ba(OH)₂ • 8H₂O), dimethylformamide (DMF), cetyltrimethyl ammonium bromide (CTAB, C₁₉H₄₂BrN), tetraethoxysilane (TEOS), ethanol acetic acid, and acetyl acetone were provided by Sinopharm Chemical Reagent Co., China.

2) PREPARATION OF BT NFs

First, the BT NFs were prepared via electrospinning. The electrospinning precursors were made up of acetic acid, barium hydroxide, strontium acetate, tetrabutyl titanate, and PVP. The injection speed of the syringe was 0.1 mm/min under an electric field of 1.5 kV/cm. The collected nanofibers were placed in a muffle furnace and calcinated at 700° for 2 h.

3) SILICA COATING OF NANO-FILLERS

The second step was to coat silica on the surface of the BT NPs or BT NFs. The ethylorthosilicate and ethanol solution (TSOS:ethanol = 1:2) was weighed and mixed well. After stirring for 2 h, silica solution A is obtained. Then, 6 ml of ammonia was measured and poured into the agitated BT NPs solution and BT NFs solution to form an alkaline environment to obtain the BT NPs solution B and BT NFs solution C. Solutions B and C were then placed in a 60 °C water bath and

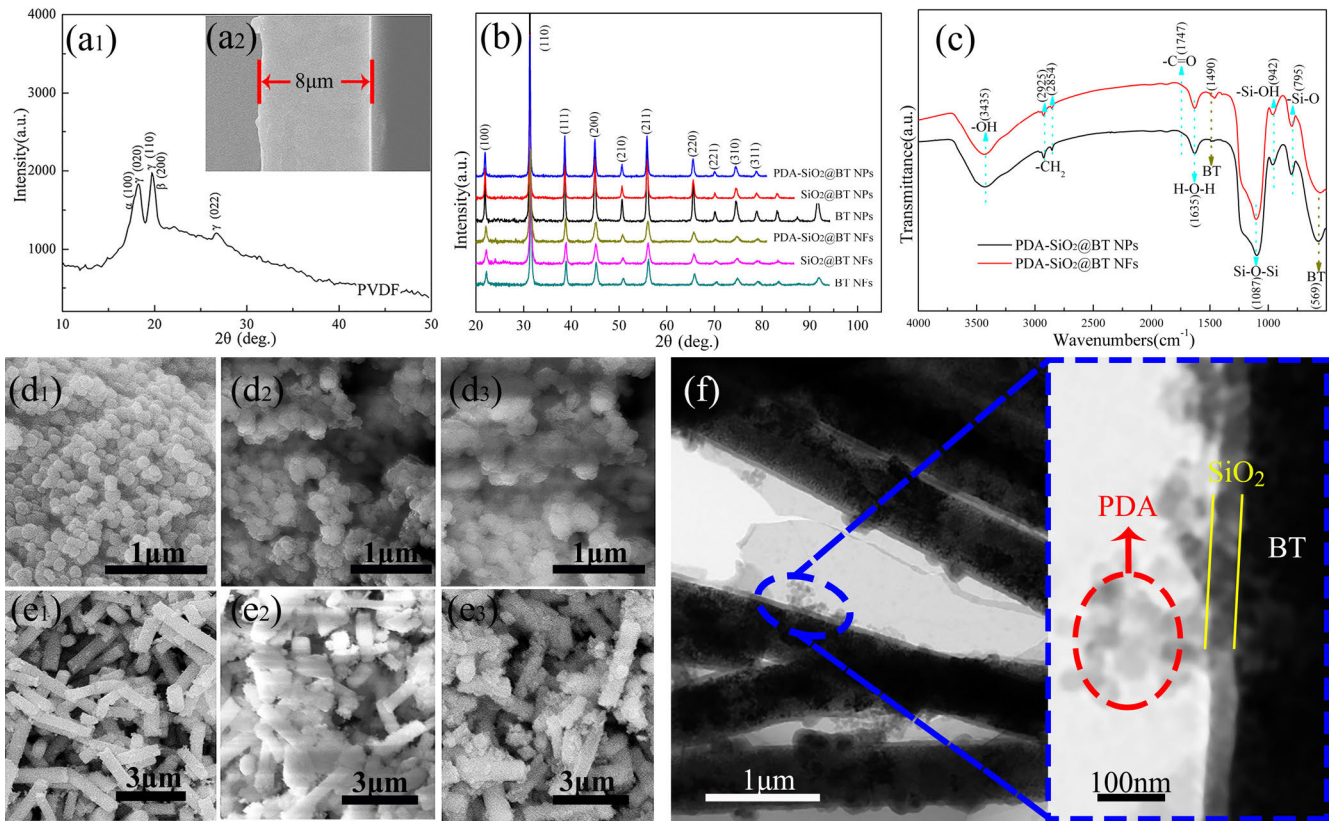


FIGURE 1. The (a₁) XRD and (a₂) SEM images of PVDF. (b) XRD patterns of BT NPs and BT NFs before and after coating SiO₂ and PDA modification. (c) FTIR spectra of PDA-SiO₂@BT NPs and PDA-SiO₂@BT NFs. (d) The SEM images of (d₁) BT NPs, (d₂) SiO₂@BT NPs and (d₃) PDA-SiO₂@BT NPs. (e) The SEM images of (e₁) BT NFs, (e₂) SiO₂@BT NFs and (e₃) PDA-SiO₂@BT NFs. (f) The TEM images of PDA-SiO₂@BT NFs.

stirred for >12 h. Then, the silicon dioxide solution A was added dropwise while stirring at a rate of 1 drop/min. Finally, the SiO₂@BT NPs and SiO₂@BT NFs were centrifuged and collected.

4) SURFACE MODIFICATION OF NANO-FILLERS

The next step was to modify the surface of the nano-fillers with PVP. Tris (hydroxymethyl) methyl aminomethane was weighed and added to 600 ml deionized water, and the pH was adjusted to 8.5 with hydrochloric acid. An appropriate amount of the SiO₂@BT NPs or SiO₂@BT NFs was added to the above solution, and it was then subjected to ultrasonic dispersion. An appropriate amount of dopamine hydrochloride was added and stirred for 12 h. After washing and drying, the PDA-SiO₂@BT NPs or PDA-SiO₂@BT NFs was obtained, and the nano-fillers with the double core-shell structure were successfully prepared at this point.

5) PREPARATION OF COMPOSITE DIELECTRICS

Finally, the prepared fillers were combined with PVDF and coated on glass substrates to finally obtain the composite films. The specific operations for this were: the BT fillers and PVDF were co-dissolved in DMF and cast to form films on the glass substrates. Next, the films were dried at 200 °C and quenched. The BT NPs/PVDF, BT NFs/PVDF, SiO₂@BT

NPs/PVDF, SiO₂@BT NFs, PDA-SiO₂@BT NPs/PVDF, and PDA-SiO₂@BT NFs/PVDF composite dielectrics were all prepared using this method.

B. MICROSTRUCTURE AND FUNCTIONAL PROPERTIES CHARACTERIZATION

For characterization and testing, the following methods and instruments were used. Field emission scanning electron microscopy (FE-SEM, Hitachi SU8020 Uhr), transmission electron microscopy (JEM-2100), X-ray diffraction (XRD) analysis (PANalytical Empyrean) and infrared spectroscopy (FTIR, JASCO 6100) were used to characterize the microstructure, crystal structure, and chemical bonds of the composite dielectrics. A broadband impedance analyzer (GmbH Novocontrol Alpha-A) was used to record the permittivity of the dielectrics. Ferroelectric hysteresis loops and breakdown strengths were obtained using a ferroelectric tester (Radiant Premier II Ferroelectric Test System with a High Voltage Power Supply).

III. RESULTS AND DISCUSSION

In this work, BaTiO₃ was selected as the filler because of its high permittivity [21], [22] and SiO₂ was employed as the coating for the BT surface. Then, the surface of the SiO₂ was further modified with PDA to improve its compatibility

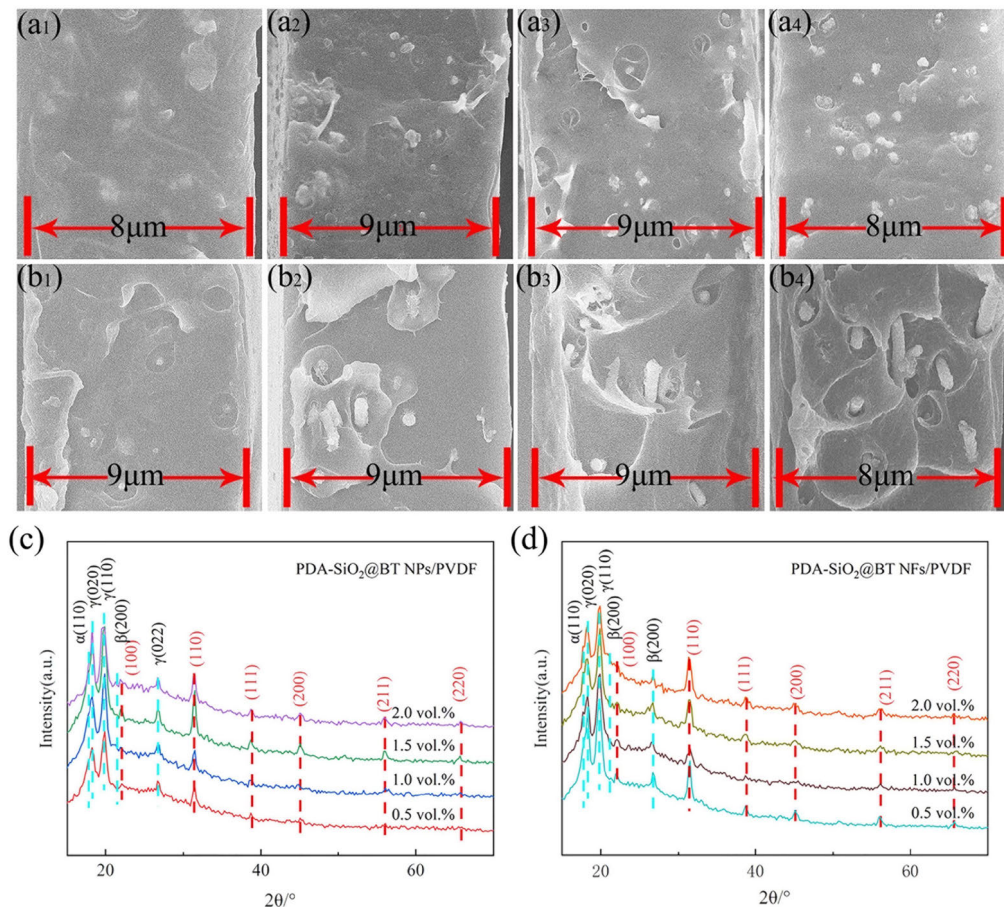


FIGURE 2. (a) The SEM images of (a₁) 0.5 vol.%, (a₂) 1 vol.%, (a₃) 1.5 vol.% and (a₄) 2 vol.% BT NPs doped PVDF-based composite dielectrics cross-section. (b) The SEM of cross-sectional morphology for the (b₁) 0.5 vol.%, (b₂) 1 vol.%, (b₃) 1.5 vol.% and (b₄) 2 vol.% BT NFs doped PVDF-based composite dielectrics. XRD patterns of (c) PDA-SiO₂@BT NPs/PVDF and (d) PDA-SiO₂@BT NFs/PVDF dielectrics in different content.

with the matrix and dispersion of the fillers. The crystal structure and microstructure of the PVDF were characterized, as shown in Figs. 1 (a₁) and (a₂), respectively, and the α (100), β (200), γ (020), γ (110), and γ (022) phases could be detected [23]. The appearance of the non-polar γ phase was induced by quenching during preparation of the composites [9]. The cross-sectional SEM image of the PVDF exhibited a dense and uniform internal structure without any defects. The crystal structures of the fillers (before and after modification) are shown in Fig. 1 (b). Only the diffraction peaks of BaTiO₃ were detected, indicating that the inorganic filler was completely crystallized and without significant impurity phases [17]. The FTIR spectra of the PDA-SiO₂@BT NPs and the PDA-SiO₂@BT NFs are shown in Fig. 1 (c). The BT and SiO₂ vibration peaks were detected and are indicated [24]. The SEM images of the BT NPs, SiO₂@BT NPs, PDA-SiO₂@BT NPs, BT NFs, SiO₂@BT NFs, and PDA-SiO₂@BT NFs are shown in Figs. 1 (d₁), (d₂), (d₃), (e₁), (e₂), and (e₃), respectively. It can be seen that the diameter of the NPs was ~ 60 nm, and the length and diameter of the NFs were ~ 2 μ m and 270 nm, respectively. In addition,

the coating and modification resulted in a slight increase of the filler size. TEM images are shown in Fig. 1 (f), and SiO₂ is marked with a yellow line and PDA is marked with a red circle. From the TEM image, clear delamination of the SiO₂ and BaTiO₃ can be observed. The silica coats the fibers evenly. The interface between PDA and silica is not clear, but scattered PDA blocks can be observed. In summary, the successful preparation of double core-shell structure fillers can be observed in Fig. 1.

The characterization results of the composite dielectric are shown in Fig. 2. The cross-sectional images in Fig. 2(a) of the composite dielectrics show a smooth and flat surface, and no impurities or defects can be observed. It should be noted that the BT NFs are aligned parallel to each other. Figures 2 (c) and (d) exhibit the crystal structure of the composite dielectrics. The characteristic diffraction peaks of the PVDF and BaTiO₃ were observed [25], which demonstrated that high-quality composite dielectrics were successfully prepared.

The two-parameter Weibull analysis was employed to investigate the breakdown strengths of dielectrics and can

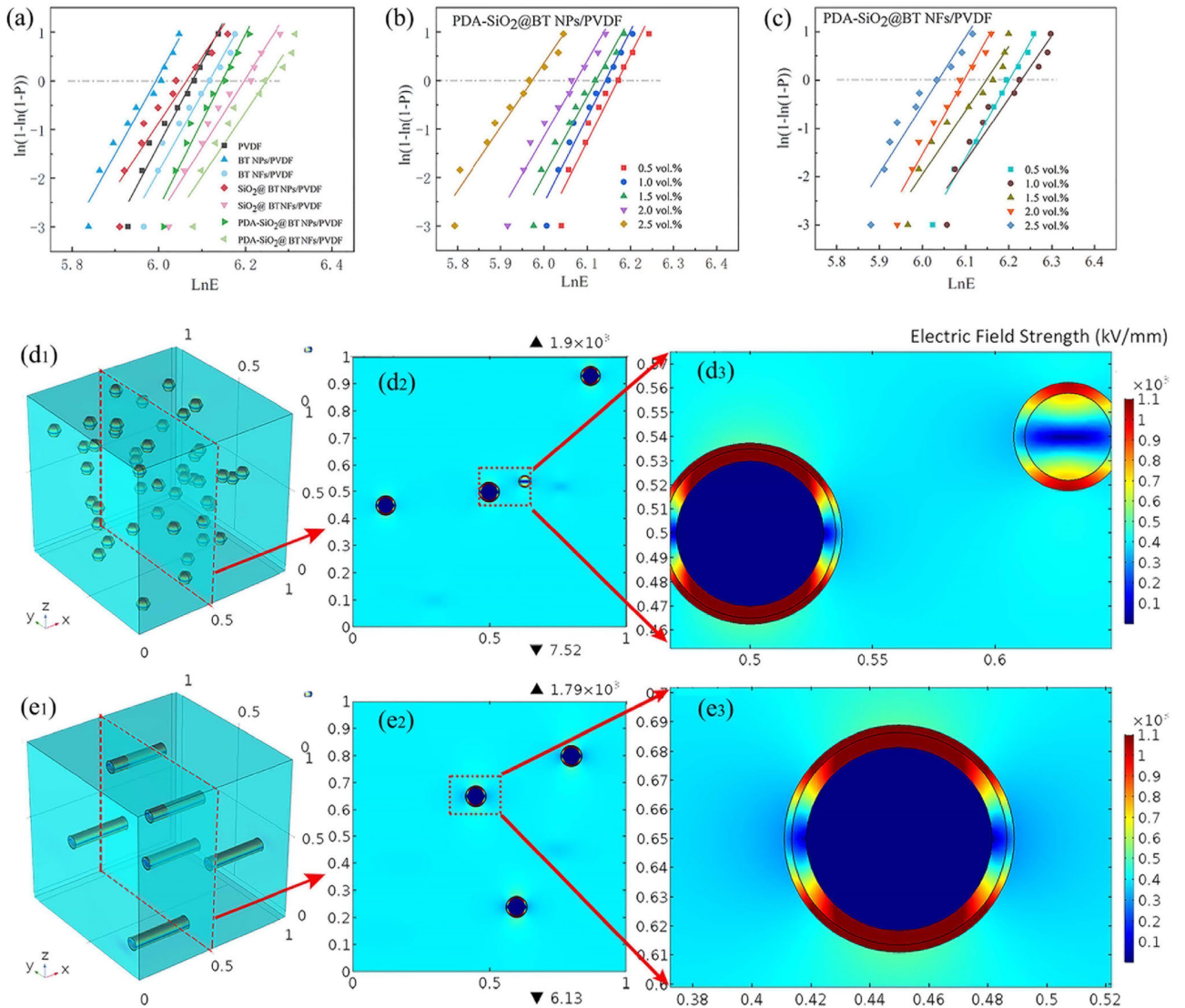


FIGURE 3. (a) The Weibull distributions of pristine PVDF and 1vol.% BT/PVDF composite dielectrics before and after surface modification. The Weibull distributions of breakdown strength for (b) PDA-SiO₂@BT NPs/PVDF and (c) PDA-SiO₂@BT NFs/PVDF. Electric field distributions obtained through finite element simulation for (d) PDA-SiO₂@BT NPs/PVDF and (e) PDA-SiO₂@BT NFs/PVDF.

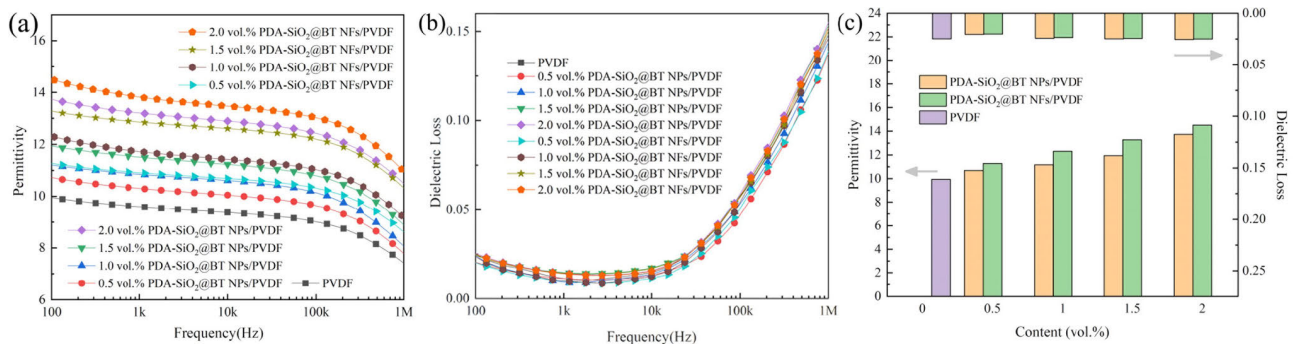


FIGURE 4. Frequency-dependent changes of (a) permittivity and (b) dielectric loss. (c) Content-dependent changes of dielectric properties at 100 Hz.

be described by: $P(E) = 1 - \exp(-(E/E_b)^\beta)$, where E is the measured breakdown strength, E_b is the characteristic breakdown strength at which the probability of

the dielectric breakdown is 63.2%, $P(E)$ is the cumulative probability of electric failure, and β is a parameter related to the reliability of the dielectrics [26]–[28].

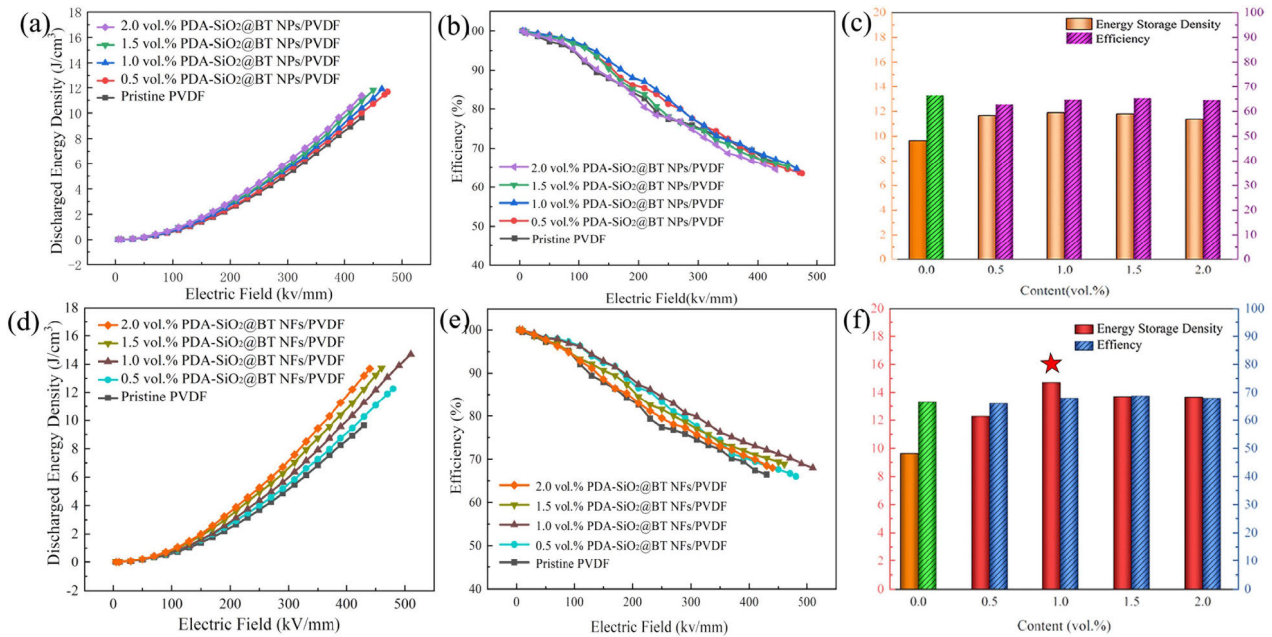


FIGURE 5. Frequency-dependent changes of (a) energy storage density and (b) charge-discharge efficiency in different amount of BT NPs. (c) The energy storage characters of BT NPs/PVDF. Frequency-dependent changes of (d) energy storage density and (e) charge-discharge efficiency in different amount of BT NFs. (f) Energy storage properties of BT NFs/PVDF.

By comparison, it can be determined that, for both the particles and the fibers, the characteristic breakdown strengths of the composite dielectrics improved after coating with silica and PDA. The E_b of the BT NPs/PVDF, SiO₂@BT NPs/PVDF, PDA-SiO₂@BT NPs/PVDF, BT NFs/PVDF, SiO₂@BT NFs/PVDF, and PDA-SiO₂@BT NFs/PVDF were 403 kV/mm ($\beta \sim 16.1$), 428 kV/mm ($\beta \sim 13.4$), 466 kV/mm ($\beta \sim 17.0$), 450 kV/mm ($\beta \sim 14.8$), 489 kV/mm ($\beta \sim 13.2$), and 520 kV/mm ($\beta \sim 15.6$), respectively. A doping of 1 vol.% BT NPs or BT NFs results in a reduction of the breakdown strength compared with the pristine PVDF because of the higher conductivity of the ceramics [29]. The double-layer core-shell structure could compensate for a decrease in the breakdown strength while retaining the dielectric properties. In addition, the characteristic breakdown strength of the composite dielectric doped double-layer core-shell structured fillers with different content were investigated. For particle doping, the E_b at 0.5 vol.%, 1 vol.%, 1.5 vol.%, 2 vol.%, and 2.5 vol.% were 478 kV/mm ($\beta \sim 17.6$), 464 kV/mm ($\beta \sim 17.4$), 451 kV/mm ($\beta \sim 16.0$), 434 kV/mm ($\beta \sim 15.2$), and 393 kV/mm ($\beta \sim 13.1$), respectively. As the content increased, the breakdown strength gradually decreased because of the introduction of carriers caused by the heavy doping. For fiber doping, the E_b at 0.5 vol.%, 1 vol.%, 1.5 vol.%, 2 vol.%, and 2.5 vol.% were 492 kV/mm ($\beta \sim 16.0$), 510 kV/mm ($\beta \sim 13.2$), 464 kV/mm ($\beta \sim 12.4$), 442 kV/mm ($\beta \sim 15.5$), and 423 kV/mm ($\beta \sim 13.4$), respectively. As the doping content increased, the breakdown electric field first increased and then decreased, which was consistent with previous reports [24]. At the same doping content, the NFs-doped composite dielectrics exhibited a higher breakdown strength

compared with the particle-filled composite. Because of the large decline in the breakdown strength, the 2.5 vol.% content sample was not considered for the subsequent studies.

Finite element analysis simulations were performed using COMSOL Multiphysics 5.2a to further explore the reasons for the observed improvements. For this model, the volume fraction of the filler was designed to be 1 vol.%. The applied electric field was 300 kV/mm and the direction was from the top to the bottom. The dimensions of the fillers are obtained from Figs. 1(e) and (f). The results of the electric field distribution showed that the shell-layer had a higher electric strength because of the lower permittivity, which is beneficial for reducing the local electric field strength in BT and PVDF, and thereby, increasing the breakdown electric field of the composite dielectrics.

The dielectric properties of composites with different compositions were investigated, as shown in Fig. 4. From Figs. 4 (a) and (b), it can be seen that the permittivities decreased with increasing frequency. The dielectric losses decreased first and then increased with increasing frequency. The permittivities and dielectric losses at 100 Hz are plotted in Fig. 4 (c) for easier observation. The permittivity increased with increasing volume fraction, which is consistent with previous results [30]–[32]. Additionally, the results showed that the PDA-SiO₂@BT NFs/PVDF had a higher permittivity and a lower dielectric loss than the PDA-SiO₂@BT NPs/PVDF, which may be attributed to the larger crystalline regions in the disordered one-dimensional fibrous fillers. This demonstrated the advantage of one-dimensional fillers for improving the dielectric properties. Considering the data from Figs. 3 and 4, it can be concluded that the composite

TABLE 1. Comparison of discharged energy density and charge-discharged efficiency in this work and related dielectric composites reported in previous literature studies.

Sample	Discharge Energy Density(J/cm ³)	Efficiency (%)	Reference
BCZT+Ag@Al ₂ O ₃ /PMMA/PVDF	9.6	69.8	[5]
MEEAA@ BT NPs/P(VDF-HFP)	7.8	-	[22]
BT@AO-DA NFs/PVDF	10.58	65	[29]
BaTiO ₃ @PMPCS/P(VDF-HFP)	7.5	56%	[32]
TiO ₂ @PZT NWS/P(VDF-TrFE-CTFE)	6.5	50%	[35]
F4CBT-1/PVDF	9.89	56%	[36]
Pt@PDA@BT/P(VDF-HFP)	6.4	52%	[37]
TSM-02	12.5	70%	[38]
BT NWS/P(VDF-CTFE)	10.8	61.4	[39]
BaTiO ₃ @TiO ₂ /P(VDF-HFP)	9.95	66	[40]
PVP@BZT NFs/PVDF	6.3	75	[41]
PDA-SiO ₂ @BT NPs/PVDF	14.7	68	This Work

dielectrics with a low doping content had enhanced breakdown strength and permittivity, which is conducive for realizing better energy storage properties.

According to equation (1), the energy storage density (U_e) can be obtained by processing the data obtained from the ferroelectric test. The charge-discharge efficiency (η) was calculated via the following formula (3):

$$\eta = U_d/U_c, \quad (3)$$

where U_d and U_c are the energy density during the discharging and charging processes, respectively [33], [34]. The calculated energy storage densities and efficiencies of the composite dielectrics are presented in Fig. 5. It can be observed that the energy storage density increased while the efficiency gradually decreased as the electric field increased. The trends of the energy storage characteristics as a function of the filler volume fraction are shown in Figs. 5 (c) and (f). The energy storage density under the maximum electric field for the 0.5 vol.%, 1.0 vol.%, 1.5 vol.% and 2.0 vol.% PDA-SiO₂@BT NPs/PVDF samples were 11.7, 11.9, 11.8, and 11.4 J/cm³. The energy storage density of the 1 vol% PDA-SiO₂@BT NPs/PVDF sample was the largest. The energy storage densities for the PDA-SiO₂@BT NFs/PVDF sample at the maximum electric field were 12.3, 14.7, 13.7 and 13.6 J/cm³ at filler contents of 0.5 vol.%, 1.0 vol.%, 1.5 vol.%, and 2.0 vol.%, respectively. Because of the synergistic effects of the breakdown strength and permittivity, the energy storage density of the composite dielectrics (NPs-doped or NFs-doped) first increased and then decreased with increasing filler content. It can be summarized from Fig. 5 that doping of the fiber leads to improved energy storage characteristics. The 1.0 vol% PDA-SiO₂@BT NFs/PVDF dielectric

had the highest energy storage density, which was a 47% improvement over the pristine PVDF material. For comparison, the performance values from related work are shown in Table 1 [34]–[41].

IV. CONCLUSION

In this work, PDA-SiO₂@BT NPs with a double core-shell structure were designed for incorporation into PVDF. The effects of SiO₂ coating and PDA surface modification on E_b of 1 vol.% BT NPs or NFs-doped PVDF were first studied. It was found that coating with silica or PDA could increase the breakdown strengths for both the NPs-doped and NFs-doped composite dielectrics. The electric field distributions inside the dielectrics were studied via finite element simulations. The results showed that the double core-shell structure allowed for the low breakdown strength portions (BT and PVDF) to bear a lower electric field. This led to a more reasonable electric field distribution and improved the overall breakdown strength. In addition, the effect of the doping content on the breakdown characteristics were studied and it was found that for the PDA-SiO₂@BT NPs/PVDF sample, the breakdown strength decreased with increasing doping content. When the doping content was increased to 2.5 vol.%, the breakdown strength of the dielectric was below that of the pristine PVDF. For the PDA-SiO₂@BT NFs/PVDF sample, the breakdown strength of the dielectric first increased and then decreased with increasing content. At a doping content of 2.5 vol.%, the breakdown strength further dropped below that of the pristine PVDF. Next, the dielectric characteristics of the PDA-SiO₂@BT/PVDF with different doping contents were explored and it was found that as the doping content increased, both the permittivity and the dielectric loss increased, which was applicable to both the NPs-doped and NFs-doped composite dielectrics. It is worth noting that the NFs-doped composite dielectric had a higher permittivity for the same content. Finally, the energy storage characteristics were investigated and it was found that doping with the double core-shell structure filler had a positive effect on the energy storage characteristics of the composite dielectric. The 1 vol.% PDA-SiO₂@PVDF had the best energy storage properties ($U_e \sim 14.7$ J/cm³ and $\eta \sim 68$ % under 510 kV/mm). Compared with the pristine PVDF, the energy storage density of the 1 vol.% PDA-SiO₂@BT NFs/PVDF sample increased by 47% under the assumption that the energy storage efficiency remained unchanged. In summary, we found an effective way to improve the energy storage characteristics of composite dielectrics by overcoming the inherent relation between the permittivity and the breakdown strength. This work may serve as a useful reference for improving the energy storage characteristics of dielectric capacitors.

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