ABSTRACT: All-organic dielectric composites are drawing increased attention owing to their high operating voltage, low loss, and superior processability. However, polymers usually possess a relatively lower dielectric constant than most other dielectrics, which seriously Suppresses the improvement of their energy density. In this work, multilayer-structured composites with excellent dielectric and energy storage properties are prepared by the stacking method, and the effect of layer numbers on the performance of the composites is studied. High-κ polymers such as poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-terfluorotrifluoroethylene-ter-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)) are used to prepare the composites with different layers. It is found that the dielectric constant is up to 14.45 at 1 kHz, which is increased with the volume fraction of the P(VDF-TrFE-CTFE) layer and layer number of the composites. Due to the increased dielectric constant, an ultrahigh discharge energy density of 18.12 J/cm³ is achieved at the electric field of 620 kV/mm. This study exhibits an effective routine to prepare flexible high-performance dielectric materials.

1. INTRODUCTION

Polymer-based dielectric composites have wide application prospects in electronic and electrical equipment, such as pulsed power equipment, grid inverters, and 5G communication, due to their advantages of high voltage endurance, flexibility, and excellent processability. At present, the commercial polymer-based dielectric capacitors are mainly based on biaxially oriented polypropylene (BOPP), of which the breakdown electric field is as high as ~640 kV/mm, while its energy density is as low as 1–2 J/cm³ due to the low dielectric constant, e.g., ~2.2. In this case, it means that the size and number of applied capacitors need to be increased to meet the energy requirements, which is contrary to the trend of miniaturization and lightweight application of devices. Therefore, to achieve higher energy storage performance, it is imperative to maintain excellent breakdown strength and improve the dielectric constant.

The energy density \( U_e \) of dielectrics can be calculated by the following eq 1

\[
U_e = \int E \, dD = \int \varepsilon_0 \varepsilon_r E \, dE
\]

where \( \varepsilon_r \) is the relative dielectric constant, \( \varepsilon_0 \) is a fixed value (vacuum dielectric constant: 8.85 × 10⁻¹² F·m⁻¹), and \( E \) is the external electric field. As shown in eq 1, to achieve a high energy storage density, the dielectrics with high dielectric constant and breakdown strength are required. One of the effective strategies is to prepare polymer-based composites with ceramics or conductive fillers. This method can indeed achieve an increase in dielectric constant due to the contribution of the high dielectric constant of inorganic fillers and enhanced interfacial polarization through improved interface area. However, not only the increased dielectric constant is based on sacrificing the breakdown strength of composites but also the flexibility of the polymer matrix is destroyed by the fillers. To increase the dielectric constant, the loading level of fillers are supposed to be as high as possible in the composites. Furthermore, there is a huge dielectric constant mismatch between the polymers (usually < 10) and fillers (usually > 1000), which brings the problem of the local concentration of electric field distribution. As a result, the breakdown strength and energy density of the dielectric composites are seriously limited.

All-organic composites are considered as an effective route to relieve the above problems. In the all-organic composites, due to their similar surface properties and dielectric properties, the challenges in the filler/polymer composites including the dispersibility, compatibility, and
local concentration of electric field distribution are significantly improved. The key question in the all-organic composites is how to improve the dielectric constant of the polymers. Ferroelectric terpolymers have a higher dielectric constant compared with most other polymers; for example, the dielectric constant of P(VDF-TrFE-CTFE) is \( \sim 50 \).41 However, the breakdown strength of these polymers is limited on the relatively low level (300–400 kV/mm) due to their high dielectric constant and polarization.36–38 In contrast, some polymers possess high breakdown strength and low dielectric constant. For example, the breakdown electric field of PVDF is as high as \( \sim 500 \) kV/mm, but its dielectric constant is only \( \sim 10 \).18 In a word, a single polymer is not ideal for energy storage in practical applications.

Recently, the strategy of combining the high breakdown strength and high dielectric constant of polymers to prepare high-performance all-organic dielectric composites was densely proposed.27–46 These works included a blending of these two polymers or preparing composites with multilayered structures. Among them, the multilayer-structured composites are usually composed of high dielectric constant polymer layers and high breakdown electric field polymer layers. It is demonstrated that the electric field distribution can be easily adjusted and the growth of electrical trees can be hindered by systematically varying the interface, structure, and content of the constituent layers.

In our previous work, PVDF-based composites with three layers were reported via the layer-by-layer solution-casting method, and the discharge energy density of the sandwich-structured composite with 25 vol % terpolymer reached 20.86 J/cm\(^3\) at an electric field of 660 kV/mm.37 Zhou et al. prepared PUA/P(VDF-CTFE) double layer composites by the casting method, of which the breakdown electric field and the efficiency were improved to be 618 kV/mm and 77%, respectively, through the action of the interface.41 Jiang et al. prepared P(VDF-HFP) and P(VDF-TrFE-CFE) multilayer-structured composites by electrosprinning.38 The electric field distribution in the composites was improved by building a multilayer interface, which improved the composites’ breakdown electric field, efficiency, and energy storage density to 600 kV/mm, 85%, and 20 J/cm\(^3\), respectively.38 It means that the polymer matrix composites with the multilayer structures have great potential in achieving high energy storage density.

In this work, all-organic composites with multilayer structure using PVDF and P(VDF-TrFE-CTFE) layers stacking alternately were prepared. The effect of the multilayer structures and the layer numbers on the properties of the dielectric composite was studied. PVDF and P(VDF-TrFE-CTFE) are chosen as the stacking layer because P(VDF-TrFE-CTFE) is a kind of fluoropolymer,18 of which the molecular structure is similar to that of PVDF homopolymer. Therefore, the compatibility problems in the composites are significantly improved. Moreover, P(VDF-TrFE-CTFE) possesses a high dielectric constant and PVDF possesses a high breakdown electric field;17 thus, the composite can combine the advantages of each other. At the same time, the structure design with PVDF as the outer layer can reduce the injection of charges, and the PVDF/P(VDF-TrFE-CTFE) interfaces can hinder the propagation of the electrical trees, which leads to the improved breakdown strength of the composites.45,51 As a result, a large energy density of 18.12 J/cm\(^3\) was achieved at 620 kV/mm. This work provided a feasible strategy to fabricate dielectric with high performance.

### 2. RESULTS AND DISCUSSION

**Figure 1** shows the cross-sectional micromorphology images of the samples. The composites have an obvious layered structure, and the interface contact between the layers is very tight without obvious holes. At the same time, each layer is evenly distributed. In the composites with three, five, and seven layers, the volume fractions of P(VDF-TrFE-CTFE) are 30, 38, and 42 vol %, respectively.

As shown in **Figure 2**, the dielectric constant of pure polymers and composites with three, five, and seven layers are, respectively, 8.96, 37.96, 11.11, 13.29, and 14.45 at 1 kHz. It can be summarized that the dielectric constant of the composites is between pure PVDF and P(VDF-TrFE-CTFE), which is increased with the number of layers at the same frequency. A much higher dielectric constant can be acquired by increasing the number of layers, which can be attributed to the increase in the loading of terpolymer. In addition, the dielectric constant of all of the samples decreases with increasing frequency, which can be attributed to the dipolar polarization of the ferroelectric polymer.18 Unlike the change in dielectric constant, the dielectric loss of the samples only slightly increases with the increase of the layer numbers and is much lower than that of pure P(VDF-TrFE-CTFE). This is because the good insulation of the PVDF outer layer can reduce the charge injection from the electrode, which can greatly reduce the leakage current of the samples. In addition, the voltage is mainly concentrated in the PVDF layers instead of the terpolymer layers, so the contribution of terpolymer to the dielectric loss is small.44,45,51 Therefore, the dielectric loss of all multilayer-structured samples is basically at the same level as PVDF.

**Figure 3** shows the variation in dielectric properties of the composites at 1 kHz in the temperature range from 25 to 120 °C. As the temperature increases, the dielectric constant and the dielectric loss of PVDF/P(VDF-TrFE-CTFE) composites are increased. For instance, the dielectric constants of the composite with a three-layer structure are 11.18 and 13.31 at the temperature of 50 and 110 °C, respectively. The reason for this phenomenon is that the high temperature will exacerbate the movement of carriers and increase the space charge polarization. At the same time, it will also cause an increase in the leakage current and aggravate the conduction loss.52
Moreover, the dielectric constant of the sample began to decrease around 115 °C, which may be attributed to the fact that P(VDF-TrFE-CTFE) began to melt.

The breakdown strength is obtained indirectly through the displacement hysteresis loops test. The characteristic breakdown strength of the samples is estimated by the Weibull distribution function

\[ P(E) = 1 - \exp\left(-\left(\frac{E}{E_b}\right)\beta\right) \]

where \( P(E) \) is the cumulative probability of the electric failure, \( E \) is the experimental breakdown strength, \( E_b \) is the characteristic breakdown strength, which refers to the breakdown strength when the cumulative failure probability is 63.2%, and \( \beta \) is a shape parameter, which evaluates the scatter of the data.53 The fitting result and its characteristic value of the breakdown electric field are presented in Figure 4.

The characteristic breakdown strength of pure PVDF, P(VDF-TrFE-CTFE), and composites with three, five, and seven layers are 542, 359, 571, 442, and 426 kV/mm, respectively. The three-layer composite exhibits a high breakdown strength, which is mainly due to two reasons.51 On the one hand, PVDF as the outer layers can provide insulation protection for the terpolymer layer and hinder the generation of electrical trees. At the same time, the interface between two different layers can block the development of electrical trees. On the other hand, the voltage will be concentrated on the PVDF layers with a low dielectric constant, which will avoid high voltage applied on the terpolymer layers. However, as the number of layers increases, the breakdown strength decreases. The main reason for this phenomenon is that as the number of layers increases, the content of P(VDF-TrFE-CTFE) with low breakdown strength also increases.
The change curve of the leakage current density at the electric field ranges from 0 to 50 kV/mm is shown in Figure 5. The leakage current of the composites with different numbers of layers changes almost the same with the electric field, and the maximum value does not exceed 0.20 μA/cm². This is consistent with the previous discussion on the change of dielectric loss with frequency. In addition, considering that the cycle performance of dielectric materials is also very important in practical applications, the performance of the composites after 10⁶ charge–discharge cycles under the conditions of 50 kV/mm and 1 kHz was tested. Its residual polarization and discharge energy density curve are shown in Figure 5b. After 10⁶ charge–discharge cycles, the performance of the composites hardly changes, which shows that its performance...
attenuation during the cycle is not obvious and they possess excellent cycle performance.

Displacement hysteresis loops of the multilayer-structured composites are shown in Figure 6a–c. The maximum breakdown electric fields of the composites with three, five, and seven layers are 620, 443, and 408 kV/mm, respectively, and the maximum polarizations are 12.57, 10.22, and 8.69 μC/cm². Although the three-layer composite has a relatively low dielectric constant, it obtains the highest maximum polarization due to the highest breakdown electric field. After the calculation based on the displacement hysteresis loops, the discharge energy density and efficiency are shown in Figure 6d. The efficiency η is calculated by η = U/cm². Although the three-layer composite has a relatively low dielectric constant, it obtains the highest maximum polarization due to the highest breakdown electric field. After the calculation based on the displacement hysteresis loops, the discharge energy density and efficiency are shown in Figure 6d. The efficiency η is calculated by η = U/cm², where U and U are the discharged and stored energy density, respectively. U and U can be obtained by integrating the discharge/charge curve on the ordinate in the displacement hysteresis loops. Since the impact of the breakdown electric field on energy density is greater than that of dielectric constant, the three-layer PVDF/P(VDF-TrFE-CTFE) composite achieves the highest discharge energy density, reaching 18.12 J/cm³. As the number of layers increases, the discharge energy density decreases accordingly, which is in accordance with the variation trend of the breakdown strength. Concurrently, the energy efficiency of the samples shows a minimum at about 200 kV/mm, which is usually related to the switching of the ferroelectric polarization in PVDF. In addition, it is found that when the electric field is low, the energy efficiency of the samples with different numbers of layers is almost the same. However, under a high electric field, the energy efficiency of the samples with more layers is higher. In particular, the energy efficiency of the seven-layer composites is almost the same as that of terpolymer and much higher than that of pure PVDF under an electric field higher than 350 kV/mm. On the one hand, the change in the low electric field confirms the previous discussion on the law of dielectric loss with frequency. On the other hand, under a high electric field, the interface induced by the multilayer structure can have a blocking effect, thereby inhibiting the transmission of carriers, reducing loss, and improving efficiency. This blocking effect becomes more obvious as the electric field increases, which may be because the motion of carriers is more vigorous under a higher electric field.

3. CONCLUSIONS

In this study, multilayer-structured PVDF/P(VDF-TrFE-CTFE) composites with high discharge energy density were prepared via a simple layer-by-layer solution-casting method. PVDF was combined with P(VDF-TrFE-CTFE) to further increase the dielectric constant of the compositions on the basis of ensuring the breakdown strength. The multilayer structure and the formed interfaces could suppress carriers’ movement; therefore, the composites maintained a low dielectric loss and leakage current density. The three-layer PVDF/P(VDF-TrFE-CTFE) composite obtained the maximum discharge energy density (18.12 J/cm³) at 620 kV/mm.

4. EXPERIMENTAL SECTION

4.1. Materials. PVDF powder (Solef-1015) was purchased from Solvay. P(VDF-TrFE-CTFE) pellets (with 7 mol % CTFE) were purchased from PolyK Technologies, LLC. Acetone (CH₃COCH₃) and N,N-dimethylformamide (DMF) solvents were provided by Sinopharm, China, and used without further purification.

4.2. Sample Preparation. Eight grams of PVDF powder and 8 g of P(VDF-TrFE-CTFE) pellets were respectively dissolved in 92 g of the mixed solvent (V_{DMF}:V_{acetone} = 3:7). The suspension was stirred at 45 °C until completely clarified. Next, the PVDF solution was cast on a glass plate and dried at 70 °C for 12 h. Then, the P(VDF-TrFE-CTFE) solution was cast on PVDF and dried again. After repeating the above steps, the polymer films of different layers (three, five, and seven) with the PVDF layer as the outer layer were obtained. Finally, the polymer films were pressed at 140 °C with 15 MPa by a flat vulcanizing machine. Pure PVDF and P(VDF-TrFE-CTFE) films were prepared in a similar process.

4.3. Characterizations. The cross-sectional micromorphology of the samples was characterized by a scanning electron microscope (SEM, JSM-6390). The gold electrodes were sputtered on both sides of the samples using metal shadow masks with a diameter of 2 mm to characterize the electrical properties. Dielectric properties of the samples were investigated using an Agilent 4294A LCR meter. The measurement was performed at room temperature and under a frequency range from 1 kHz to 10 MHz. High-temperature dielectric properties were carried out through a high-temperature dielectric temperature spectrum measurement system (DMS-500) at 1 kHz with a temperature range from 25 to 120 °C. The displacement hysteresis loops and the leakage current of the samples were characterized using a TF Analyzer 2000 series (aixACT, Germany) and a Delta 9023 high-temperature furnace at room temperature and 10 Hz.

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Notes
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