Concurrent Enhancement of Breakdown Strength and Dielectric Constant in Poly(vinylidene Fluoride) Film with High Energy Storage Density by Ultraviolet Irradiation

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ABSTRACT: Polyvinylidene fluoride (PVDF) film with high energy storage density has exhibited great potential for applications in modern electronics, particle accelerators, and pulsed lasers. Typically, dielectric/ferroelectric properties of PVDF film have been tailored for energy storage through stretching, annealing, and defect modification. Here, PVDF films were prepared by the solution casting method followed by an ultraviolet (UV) irradiation process, with special emphasis on how such treatment influences their dielectric and energy storage properties. Upon UV irradiation, the dielectric constant and breakdown strength of the PVDF film were enhanced simultaneously. A high energy density of 18.6 J/cm$^3$, along with a charge–discharge efficiency of 81% at 600 MV/m, was achieved in PVDF after exposure to UV for 15 min. This work may provide a simple and yet effective route to enhance energy storage density of PVDF-based polymers.

1. INTRODUCTION

Dielectric polymer capacitors possessing high power density capacity and fast discharge capability have recently gained great attention in modern electronics and electrical power systems.$^{1-3}$ However, compared with the supercapacitors and lithium-ion batteries, low energy density is one of the major challenges on the increasing demands of micro-electronics and electric power systems. For example, the energy density of most widely used polypropylene (BOPP) is limited to 1–2 J/cm$^3$.$^{3,4}$ Dielectric polymer materials can store and release energy with reversibility of polarization after removing the electric field. In general, the energy storage density ($U_e$) of dielectric materials can be expressed as follows:

$$U_e = -\int_{D_{max}}^{D} EdD$$

(1)

where $E$ denotes the electric field and $D$ represents the electrical displacement. Specifically, for linear dielectrics, eq 1 could be described as

$$U_e = 1/2\varepsilon_0\varepsilon_r E_b^2$$

(2)

where $\varepsilon_0$ and $\varepsilon_r$ represent vacuum dielectric permittivity and relative dielectric permittivity, respectively. $E_b$ is the breakdown strength of the dielectric material.$^{5,6}$ Apparently, the energy density strongly depends on $E_b$, which makes polymer-based dielectrics an ideal choice owing to their much higher $E_b$ than their ceramic counterparts.$^7$ Among multitudinous dielectric materials, PVDF displays obvious advantages including easy processing, good flexibility, and high dielectric constants.$^8$ Compared to the linear polymer, non-linear ones with polar groups in the molecular chain usually exhibit higher $\varepsilon_r$. Moreover, the fluorine atoms in the PVDF molecular chain have larger electronegativity and smaller size, leading to larger dipole moment. However, PVDF possesses relatively low energy storage density and high energy loss due to the high remnant polarization.$^9$

The structural optimization has proved to be an effective method to improve the dielectric and ferroelectric properties of polymers. Several studies on the crystal modification of PVDF, such as stretching, annealing, cross-linking, and defect modification, have been reported.$^{9-12}$ For instance, by introducing other monomers into PVDF polymer chains, higher polarization and strong dipole field interactions could be achieved, and the ferroelectric hysteresis loss is reduced.$^{13}$ Several monomers such as chlorotrifluoroethylene (CFE), trifluoroethylene (TrFE), chlorotrifluoroethylene (CTFE), and hexafluoroethylene (HFP) have been introduced to the VDF chains in PVDF. For example, the addition of an HFP monomer can greatly improve the mechanical properties of the polymer; a large $E_b$ of >700 MV/m can be obtained in P(VDF-
HFP), yielding the highest energy density over 25 J/cm³. However, modifying PVDF still exhibit moderate discharged efficiency (η) below 70%. It has been widely reported that the ferroelectric loss of PVDF-based polymers is closely related to its matrix phase structure. In details, compared with the non-polar α phase of the zigzag configuration, PVDF shows greater dielectric loss in the polar β-phase of the all-trans configuration. Interestingly, high-energy radiation can effectively reduce the ferroelectric domain size of PVDF-based polymers and facilitate the transformation of PVDF into a relaxor ferroelectric, where the dipoles revert and respond rapidly to the external electrical field with greatly reduced dielectric loss. Moreover, high-energy radiation can improve the crystallinity in polymer materials and lead to the formation of a cross-linked network, thereby improving the dielectric/ferroelectric properties of PVDF. Very recently, Chen et al. reported that the εr of the PP film was greatly enhanced by UV irradiation, which resulted in chain scission and cross-linking. Such an observation inspired us to explore the influence of ultraviolet radiation on the energy storage performance of the PVDF system.

In this work, we reported the simultaneously enhanced breakdown strength and dielectric constant in PVDF after exposure to UV irradiation. The UV irradiation can increase the ε, up to 15 and E_b to 637 MV/m, resulting in great enhancements of 43 and 26% as compared with the untreated PVDF, respectively. The UV-irradiated PVDF films still maintained a high energy efficiency η of 81% and stable performance over a charge–discharge cycling of 10⁶ cycles even under high electric fields. Our results shed light on enhancing the energy storage capacity of PVDF-based dielectrics via UV irradiation for application in electrical power systems and microelectronics.

2. EXPERIMENTAL SECTION

2.1. Preparation of PVDF Film. PVDF (99.99%, Arkema) powders were first dispersed into 4 mL N,N-dimethylformamide (DMF) (99.5%, Sigma). After stirring for 2 h, a homogeneous solution was obtained. Subsequently, the solution was casted on a clean glass plate. After drying under vacuum at 60 °C for 12 h, the PVDF films were immediately quenched in ice water by heating at 200 °C for another 10 min followed by drying at 40 °C for 12 h. Finally, the obtained PVDF films with a thickness of 10–12 μm were peeled off from the glass plate.

2.2. UV Irradiation Treatment. For the UV irradiation, each side of PVDF films was irradiated at room temperature for 5–20 min, with an irradiance intensity of 20 mW/cm². The irradiation source was located at 5 cm from the PVDF films. To investigate the effect of UV irradiation on dielectric performance, each side of the pristine PVDF films was exposed to UV irradiation for 5, 10, 15, and 20 min, and the resultant samples were termed as PVDF-UV-5 min, PVDF-UV-10 min, PVDF-UV-15 min, and PVDF-UV-20 min, respectively.

2.3. Material Characterization. UV irradiation experiments were performed via the UV lamp system (200 W, λ_{max} = 185 and 254 nm, BOT-UV200WT). Crystal information of PVDF film was characterized by X-ray diffraction (XRD) (Rigaku SmartLab) using Cu Kα radiation. Atomic force microscopy (AFM) (Asylum research Cipher ES) was employed to examine the morphology of the PVDF films. Structural information of the PVDF films was carried out using Fourier transform infrared (FTIR) spectroscopy (Nicolet Nexus). Melting behavior analysis of the PVDF films was performed by heating to 220 °C at a rate of 10 °C/min using a differential scanning calorimeter (DSC 8500, PerkinElmer). For the swelling characterization, the rate of insolubility of the prepared samples was calculated from the weight decrease in 20 mL of DMF solution for 2 h. The surface composition was carried out by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fisher Scientific). For the electrical measurement, copper electrodes (3 mm in diameter and 50 nm in thickness) were deposited on both sides of the PVDF films. Dielectric properties of PVDF films were measured via an LCR meter (Agilent 4294A) at room temperature in a frequency range of 10⁴ to 10⁶ Hz at 1 voltage of root mean square. Square displacement–electric field (D–E) loops were measured at 10 Hz using a ferroelectric testing system (CPE1701, PolyK Technologies). Electric breakdown strength was evaluated via the dielectric withstand voltage test (Beijing Electro-mechanical Research Institute Supervoltage Technique) at a ramping rate of 200 V/s and a limit current of 2 mA. The DC leakage current densities (in A/cm²) were collected with the ferroelectric test system. Charge and discharge experiments were carried out via a capacitor charge–discharge test system (PKCP1701, PolyK Technologies) with a high-voltage MOSFET switch, where the samples were charged by an electric field of 200 MV/m through the MOSFET switch and the stored energy was discharged to a load resistor of 100 kΩ.

3. RESULTS AND DISCUSSION

As shown in Figure 1a, the fluorine and hydrogen atoms in the branched chains were connected to the carbon atoms in the
PVDF films to UV irradiation ruptured the covalent bonds to form the free radicals, which were associated with the formation of a CF═O group (Figure 1c).18 In addition, DSC curves provided additional information to determine the chemical structure of the PVDF film (Figure 1d). Compared to the pristine PVDF, the melting point of irradiated PVDF gradually decreased with the increasing UV irradiation time, leading to the enhanced molecular chain mobility after UV irradiation. In contrast, the crystallinity of the PVDF films gradually increased from 50 to approximately 65.5% when the UV irradiation time was extended up to 20 min (Table 1). In this context, the extension of UV irradiation accelerated the breakage of molecular chain, thereby increasing the degree of crystallinity in the PVDF films.19–21

| sample              | \(T_m\) (°C) | \(\Delta H_f\) (J/g) | \(X_c\) (%) |
|---------------------|--------------|----------------------|-------------|
| untreated PVDF      | 165.7        | 52.6                 | 50          |
| PVDF-UV 5 min       | 163.5        | 59.4                 | 56.7        |
| PVDF-UV 10 min      | 163.6        | 58.2                 | 53.6        |
| PVDF-UV 15 min      | 163.0        | 61.4                 | 58.6        |
| PVDF-UV 20 min      | 162.0        | 68.6                 | 65.5        |

AFM images of the pristine PVDF and PVDF film irradiated for different times are shown in Figure 2. The surface of pristine PVDF was smooth, with a root mean square (RMS) roughness of 3.4 nm. After UV irradiation for 5 min, however, the surface became much rougher and the RMS roughness was increased to about 10.5 nm, which could be attributed to the uneven molecular weight caused by free radical polymerization. With further exposure to UV irradiation, the RMS roughness reached 16.6 nm in PVDF-UV-10 min, as depicted in Figure 2c. The maximum RMS roughness of 21.9 nm was achieved in the PVDF-UV-20 min (Figure 2d), suggesting the excessive degradation of the PVDF film.

Chemical compositions of the PVDF films were further analyzed by XPS (Supporting Information, Figure S1). A new signal indicative of the O element confirmed the existence of chain scission in the PVDF-UV-15 min. The C 1s spectrum for the irradiated PVDF (Figure S1b) was fitted with four peaks, which correspond to different types of carbon bonds, that is, a C–C peak at 284.5 eV, a C–H peak at 286.4 eV, a C–OH peak at 289.3 eV, and a C–F peak at 291 eV.22 As compared to pristine PVDF film, the appearance of C═O (532 eV), C–OH (533 eV), and O–CF (535.7 eV) bonds in the O 1s spectrum confirmed the chain scission occurring in the PVDF-UV-15 min. This result suggests the formation of oxygen-containing groups in the near-surface layer of PVDF film after UV irradiation, primarily owing to interaction of polymer molecules with \(O_2\) in air (Figure S1c).

Frequency-dependent dielectric performance is depicted in Figure 3. Due to the interfacial polarization relaxation of PVDF film, the \(\varepsilon_r\) monotonically decreased with the increase of frequency (Figure 3a).23,24 Notably, the \(\varepsilon_r\) kept rising with extended exposure to UV irradiation in all samples. For example, the \(\varepsilon_r\) values of pristine PVDF and PVDF-UV films at 100 Hz were 10.5 and in the range of 12.3–15.0, respectively. The enhancement was about 17%, and about 26.6%–43% with the monotonous increase in UV irradiation time. Such enhancement in the \(\varepsilon_r\) after UV irradiation can be attributed to the detachment of side groups and the formation of C–O bonds, which prompt ionic polarization and dipole mobility in PVDF. Meanwhile, the dielectric loss slightly increased with the extension of UV exposure time, which may be related to the high conductivity and relaxation loss induced by the polar groups. Moreover, a slight decrease in \(\varepsilon_r\) was observed with further increase in the irradiation time up to 20 min. This can be mainly attributed to the defects induced by the excessive exposure to UV radiation, resulting in a decrease in the dipole mobility (Figure 3b).

Figure 4 displays the leakage current density of PVDF films. In general, the leakage current densities were maintained within the range of \(10^{-10}\) to \(10^{-8}\) A cm⁻² under the electric field of 200 MV m⁻¹. For pristine PVDF films, the leakage current density was \(5.49 \times 10^{-7}\) A cm⁻² at 200 MV m⁻¹. The increased crystallinity may be responsible for reduced leakage current density to \(4.5 \times 10^{-7}\) A cm⁻² with UV irradiation up to 5 min, above which substantially increased leakage current
density could be observed. For example, the leakage current densities of PVDF-UV-10 min and PVDF-UV-15 min films were \(8.54 \times 10^{-7}\) and \(9.83 \times 10^{-7}\) A cm\(^{-2}\) at 200 MV m\(^{-1}\), respectively. The slightly enhanced leakage density could be associated with the formation of a large number of charged radicals generated by breaking of chemical bonds.\(^{25}\) With irradiation time up to 20 min, a further increased leakage current density of \(1.48 \times 10^{-6}\) A cm\(^{-2}\) was observed.

As expected, an enhanced \(E_b\) was critical to the improvement of energy storage density in dielectric materials. The \(E_b\) was calculated from Weibull statistics and is shown in Figure 5a.

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

where \(P(E)\), \(E_b\), and \(\beta\) are the cumulative probability of the electric failure, the characteristic breakdown strength corresponding to 63.2% probability of failure, and shape parameter, respectively.\(^{26-29}\) Obviously, UV irradiation was effective to improve the \(E_b\) of the PVDF films. For example, the \(E_b\) increased from 507 MV/m in the pristine PVDF film to 529 MV/m in the PVDF-UV-5 min and then increased to 589 MV/m in the PVDF-UV-15 min. Specially, cross-linking and the increase of crystallinity during UV irradiation played an important role in improving the \(E_b\) of the PVDF films.

The solubility of PVDF in DMF was carried out to evaluate the effect of UV irradiation on its chains. As shown in Figure S2, the pristine PVDF was fully soluble in DMF. However, the insoluble fraction of PVDF in DMF gradually increased with UV irradiation time. For example, the insoluble fraction was increased to 44 wt % with UV irradiation for 15 min, which could be attributed to cross-linking in PVDF. After extended UV irradiation up to 20 min, the insoluble fraction was decreased to 33 wt %. This result suggests that PVDF films underwent both chain scission and degradation instead of cross-linking. Therefore, the maximum \(E_b\) of \(~637\) MV/m was obtained in the PVDF-UV-15 min, much higher than that of \(507\) MV/m for the pristine PVDF film. However, a further increase of UV irradiation time to 20 min caused a decrease in the \(E_b\), which could be ascribed to excessive cross-linking and degradation in the PVDF films (Figure 5b).\(^{11}\)

Unipolar \(D-E\) loops of PVDF irradiated under different times are shown in Figure 5c. With increasing UV irradiation time, the enhancement of maximum polarization was observed, which could be ascribed to the improved \(E_b\). In addition, \(P_{\text{max}}\) of the PVDF-UV-15 min was about \(8.1\) \(\mu\)C/cm\(^2\), showing an increment of \(37\%\) as compared with \(5.9\) \(\mu\)C/cm\(^2\) observed in the untreated PVDF. Meanwhile, the PVDF films after UV irradiation still maintained a relatively lower remnant polarization. The discharged energy density and charge–discharge efficiency are displayed in Figure 5d,e. The untreated PVDF presented the lowest discharge energy density of \(11.4\) J/cm\(^3\) with a \(\eta\) of 81%. As shown in Figure 5f, benefitting from the enhanced \(E_b\) and \(\varepsilon_r\), PVDF-UV films exhibited greatly improved energy storage performance. In detail, the maximum discharged energy density of \(18.6\) J/cm\(^3\) was achieved in PVDF-UV-15 min. However, further elongation of UV irradiation time would result in reduced \(U_c\) as a consequence of the decreased \(E_b\) in the PVDF-UV-20 min. More importantly, the PVDF-UV-15 min maintained a high \(\eta\) of 81% even at 600 MV/m, probably owing to the improved crystallinity of the PVDF and reduction in the defect concentrations after UV irradiation.

To further demonstrate the stability of the PVDF-UV film as the dielectric energy storage medium, the cyclic fast-discharge experiment of the pristine PVDF and the PVDF-UV-15 min film was performed at 400 MV/m. As in Figure 6a, both energy

**Figure 4.** Leakage current density of the pristine PVDF and PVDF irradiated by UV for different times.

**Figure 5.** (a) Weibull statistic of breakdown strength for the pristine PVDF and irradiated PVDF. (b) Plot of Weibull breakdown strength of the PVDF with UV irradiation time. (c) Unipolar \(D-E\) loops obtained at 10 Hz. Plots of (d) discharged energy density and (e) energy storage efficiency with electric field. (f) Plots of discharged energy density and charge–discharge efficiency with UV irradiation time.
density and $\eta$ exhibited stable performance without obvious degradation over a charge–discharge cycling up to $10^6$ cycles, showing a high stability of the PVDF-UV-15 min film. Furthermore, a fast discharge time was required in high power capacitors. A fast discharge test was implemented. The discharged energy density ($U_e$) of a dielectric capacitor could be calculated using the following expression:

$$U_e = R \int (t) \frac{dt}{V}$$

where $R$ and $V$ represent the load resistance (100 kΩ) and the sample volume, respectively. The discharged time was determined as the time required to release 90% of the final stored energy.\(^{10}\) As depicted in Figure 6b, the PVDF-UV-15 min film liberated an energy density of 0.89 J/cm$^3$ at 200 MV/m, while the discharged time was only 13.9 ms, which exhibited a faster discharge rate compared with 14.8 μs of the pristine PVDF. Accordingly, the PVDF-UV-15 min film exhibited a superior power density of 0.068 MW/cm$^3$, which was 1.5 times higher than 0.045 MW/cm$^3$ of the pristine PVDF. These results showed good potential of these UV-irradiated PVDF films for applications in high energy density capacitors.

4. CONCLUSIONS

In summary, proper UV irradiation can significantly enhance the energy storage capacity of the PVDF film. Upon UV irradiation, scission and cross-linking occurred in PVDF, and therefore, contribute to simultaneous enhancement in the dielectric constant and breakdown strength. Compared with untreated PVDF film, the UV-irradiated PVDF films exhibited a remarkably high discharged energy density of 18.6 J/cm$^3$ and a moderate charge–discharge efficiency of 81%. Stable performance can also maintain over a charge–discharge cycling up to $10^6$ cycles even under high electric field. This work may offer a simple route to improve energy storage performance of various ferroelectric polymers through UV irradiation, which held promise for mass production.

ASSOCIATED CONTENT

 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07373.

XPS spectra of PVDF films and solubility of PVDF films in DMF with UV irradiations for different times (PDF)

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Notes
The authors declare no competing financial interest.

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