



Dielectric, Polarization, and Energy-Storage Response of Solution-Cast PVDF/Ba_{0.8}Ca_{0.2}(Zr_{0.1}Ti_{0.9})O₃ Composite Films

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Abstract

Poly(vinylidene fluoride) (PVDF) composite films filled with lead-free Ba_{0.8}Ca_{0.2}(Zr_{0.1}Ti_{0.9})O₃ (BCZT) were prepared by solution casting, using ceramic powder made by solid-state reaction. From the weighed masses, the dry films contain 9–50 wt.% BCZT. X-ray diffraction shows semi-crystalline PVDF together with crystalline perovskite BCZT. At room temperature the relative permittivity falls with frequency for every composition and does not change monotonically with ceramic fraction. The 37.5 wt.% film has the largest permittivity, dropping from about 11.5 at the low-frequency end of the sweep to 8.2 at 5 MHz, with $\tan \delta$ between 0.08 and 0.13. Polarization–electric-field (P – E) loops measured at a common field of 100 kV cm^{−1} are slim and unsaturated; at this field the 37.5 wt.% film gives the largest maximum polarization (0.25 μC cm^{−2}) and recoverable energy density (0.0106 J cm^{−3}), and the efficiency is 79–83% up to 37.5 wt.% and 70%

at 50 wt.%. At the highest field recorded for each film, the 9 wt.% film reaches $W_{\text{rec}} = 0.145 \text{ J cm}^{-3}$ at 700 kV cm^{−1}, and among these maximum-field loops the 28.6 wt.% film has the highest efficiency, 73.9% at 300 kV cm^{−1}. Since the maximum field differs from film to film, the maximum-field values are reported as loop-specific results and not as a ranking of compositions.

Keywords: PVDF, BCZT, polymer-ceramic composite, dielectric permittivity, P – E loop, energy storage.

1 Introduction

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline fluoropolymer with comparatively high dielectric strength, low density, chemical stability, solution processability, and electroactive behavior. It crystallizes in several polymorphs, and the polar β and γ phases are the ones of interest for dielectric, piezoelectric, and ferroelectric applications. Which phases form depends on processing history, solvent, thermal treatment, mechanical deformation, and electrical poling [1]. Polymer dielectrics are attractive for electrical energy storage because a high breakdown



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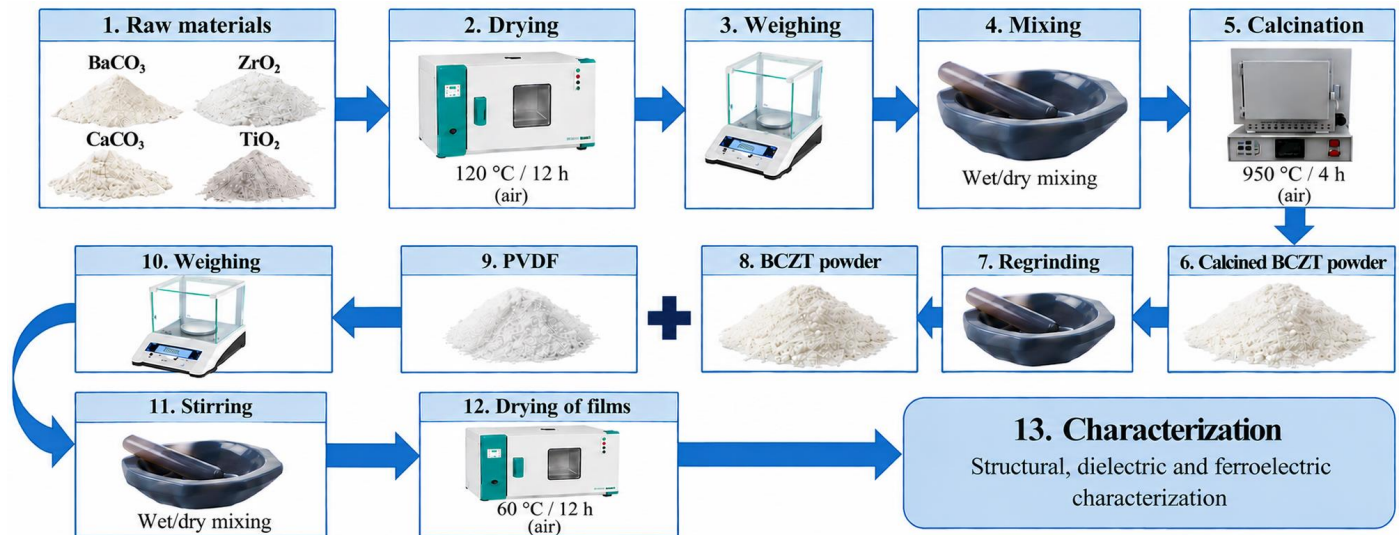


Figure 1. Schematic of the solid-state synthesis of BCZT powder and the preparation of the PVDF/BCZT composite.

field partly offsets their modest relative permittivity; the recoverable energy density and efficiency, however, depend jointly on polarization, hysteresis loss, and the maximum field the material can sustain [2].

A common way to raise the dielectric response of PVDF is to disperse a high-permittivity ceramic filler in the polymer. Work on $\text{BaTiO}_3/\text{PVDF}$ and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{PVDF}$ has shown that the ceramic raises the effective permittivity, but that the result also depends on particle dispersion, interfacial electrical contrast, filler fraction, and field concentration in the heterogeneous composite [3, 4]. There is a trade-off: more ceramic may increase polarization while lowering the field the composite can tolerate, so permittivity alone is not a sufficient measure of energy-storage performance. BCZT/PVDF composites have been studied with particulate fillers, morphotropic-phase-boundary compositions, and BZT–BCT nanofibers [5–10], and more recently as solution-cast or tape-cast films for dielectric and piezoelectric use [11–13]. These reports show that the response depends strongly on ceramic composition, filler fraction, morphology, and processing route.

The ceramic used here, $\text{Ba}_{0.8}\text{Ca}_{0.2}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$, belongs to the composition-sensitive $\text{Ba}_{1-x}\text{Ca}_x(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ system, whose structural phase-transition sequence and electrocaloric behavior have been characterized as functions of x [14, 15], and has been used as a PVDF filler less often than the $x \approx 0.14$ – 0.15 and morphotropic-phase-boundary-derived BCZT formulations. In this work we prepare solution-cast PVDF films with five BCZT loadings and report their

X-ray diffraction patterns, their relative permittivity and dielectric loss up to 5 MHz, and their P – E loops. The loops are compared at a common field of 100 kV cm^{-1} ; loops taken at higher fields are reported separately for each film.

2 Experimental Procedure

Figure 1 outlines the synthesis of BCZT and the preparation of the PVDF/BCZT films. BCZT powder was made by conventional solid-state reaction. BaCO_3 , CaCO_3 , ZrO_2 , and TiO_2 powders (stated purity above 99%) were dried at 120°C for 12 h and weighed in the stoichiometric ratio of the target composition. The mixture was wet-ground in a mortar and pestle for 3 h in a volatile organic medium, dried, and transferred to alumina crucibles. Calcination was carried out at 950°C for 4 h. After cooling, the calcined powder was re-ground for 1 h, dried, and sieved before the films were prepared.

For each formulation, 0.50 g of PVDF was dissolved in 50 mL of *N,N*-dimethylformamide (DMF) by magnetic stirring at 70°C and 650 rpm for 6 h. The required mass of BCZT powder was then added gradually, and the suspension was stirred for a further 2 h and ultrasonicated for 30 min. The mixture was cast into a clean Petri dish and dried at 80°C for 12 h. The free-standing film was then peeled off and kept in a desiccator until characterization. The BCZT masses were 0.05, 0.10, 0.20, 0.30, and 0.50 g for a fixed PVDF mass of 0.50 g, corresponding to 9.1, 16.7, 28.6, 37.5, and 50 wt.% BCZT in the dry film; the 9.1 wt.% composition is referred to throughout as 9 wt.% for brevity.

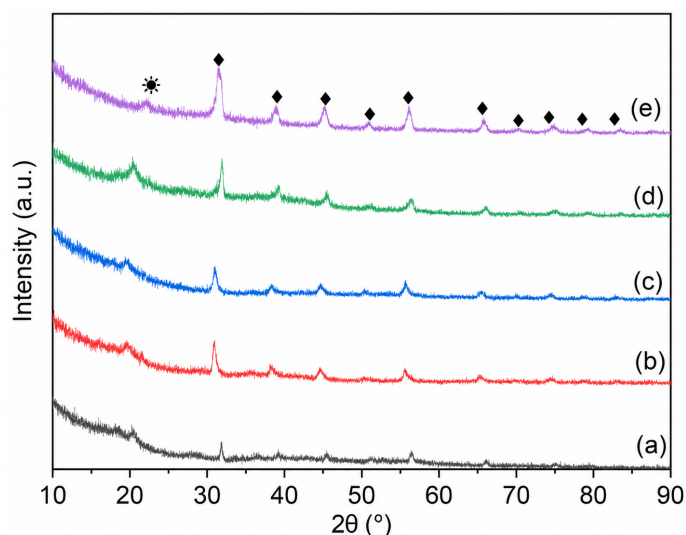


Figure 2. XRD patterns of PVDF/BCZT composite films containing (a) 9, (b) 16.7, (c) 28.6, (d) 37.5, and (e) 50 wt.% BCZT.

X-ray diffraction (XRD) patterns were collected with Cu K α radiation over $2\theta = 10\text{--}90^\circ$, evaluated with WinXPOW, and compared with standard diffraction data for the constituent phases. XRD was used only to check phase consistency; no full-pattern refinement was carried out. Film thickness was measured at several positions with a digital micrometer, and the mean value was used in the electrical calculations. The room-temperature relative permittivity (ϵ_r) and loss tangent ($\tan \delta$) were measured as functions of frequency up to 5 MHz.

P – E loops were recorded at progressively increasing field amplitude. A loop at 100 kV cm^{-1} is available for every film, and this field is used to compare the compositions. The highest field reached differs from film to film; it is simply the last amplitude in the available measurement series, was not set by a common breakdown protocol, and should not be read as a breakdown strength. Energy-storage quantities were obtained in Origin by numerical integration of the charging and discharging branches, both for the 100 kV cm^{-1} loops and for the highest-field loop of each film.

3 Results and Discussion

Figure 2 shows the XRD patterns of the five films. A broad polymer feature appears at about $18\text{--}21^\circ$, as expected for semi-crystalline PVDF. Reflections of the α , β , and γ polymorphs overlap in this range, so these patterns cannot give the fractions of the individual polymorphs [1, 16]; that would need a complementary method such as FTIR with phase-sensitive vibrational

bands. Sharp reflections (marked ◆) at about 31° , 39° , 45° , 51° , 56° , and 66° , with weaker ones between 70° and 83° , survive film fabrication and match crystalline perovskite BCZT. They grow relative to the polymer feature as the ceramic fraction increases, which reflects the larger amount of diffracting ceramic and not a change in intrinsic crystallinity. Some patterns show weak features near the background, but the scan quality does not allow them to be assigned to a secondary phase. The patterns also do not resolve the room-temperature symmetry of the BCZT phase, whose structure is sensitive to composition across the $\text{Ba}_{1-x}\text{Ca}_x(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ system [14, 15].

The room-temperature dielectric response up to 5 MHz is shown in Figure 3. The relative permittivity falls with increasing frequency for every film. Read from the plots, ϵ_r goes from about 2.4 to 2.0 for 9 wt.% BCZT, 9.0 to 6.8 for 16.7 wt.%, 3.5 to 2.8 for 28.6 wt.%, 11.5 to 8.2 for 37.5 wt.%, and 7.3 to 5.8 for 50 wt.%. The 37.5 wt.% film has the highest permittivity over most of the range. This dispersion is what one expects when the slower polarization processes can no longer follow the alternating field, although the data do not single out one relaxation mechanism. The loss tangent also depends on composition: over most of the range $\tan \delta$ is about 0.07–0.10 for 9 wt.%, 0.08–0.15 for 16.7 wt.%, 0.08–0.09 for 28.6 wt.%, 0.08–0.13 for 37.5 wt.%, and 0.06–0.10 for 50 wt.%.

Neither ϵ_r nor $\tan \delta$ varies monotonically with ceramic fraction. The large differences between neighboring compositions, in particular the low ϵ_r of the 28.6 wt.% film next to the 16.7 and 37.5 wt.% films, may come from differences in how the BCZT particles are distributed in the PVDF matrix. Agglomeration, polymer–ceramic interfacial area, and the film microstructure left by casting and solvent evaporation all change the local field distribution and the interfacial polarization, and hence the effective permittivity. The crystalline-phase distribution of the PVDF may differ between films as well. Filler dispersion and polymorph fractions were not measured here, so these contributions cannot be separated and we do not assign the non-monotonic behavior to one mechanism. Some earlier PVDF/BCZT studies reported an overall rise in permittivity with filler content [11, 13]; the difference shows how strongly the response depends on ceramic composition, filler state, film geometry, and processing history.

Figure 4 shows the P – E loops recorded at increasing field amplitude. At 100 kV cm^{-1} , where all five films

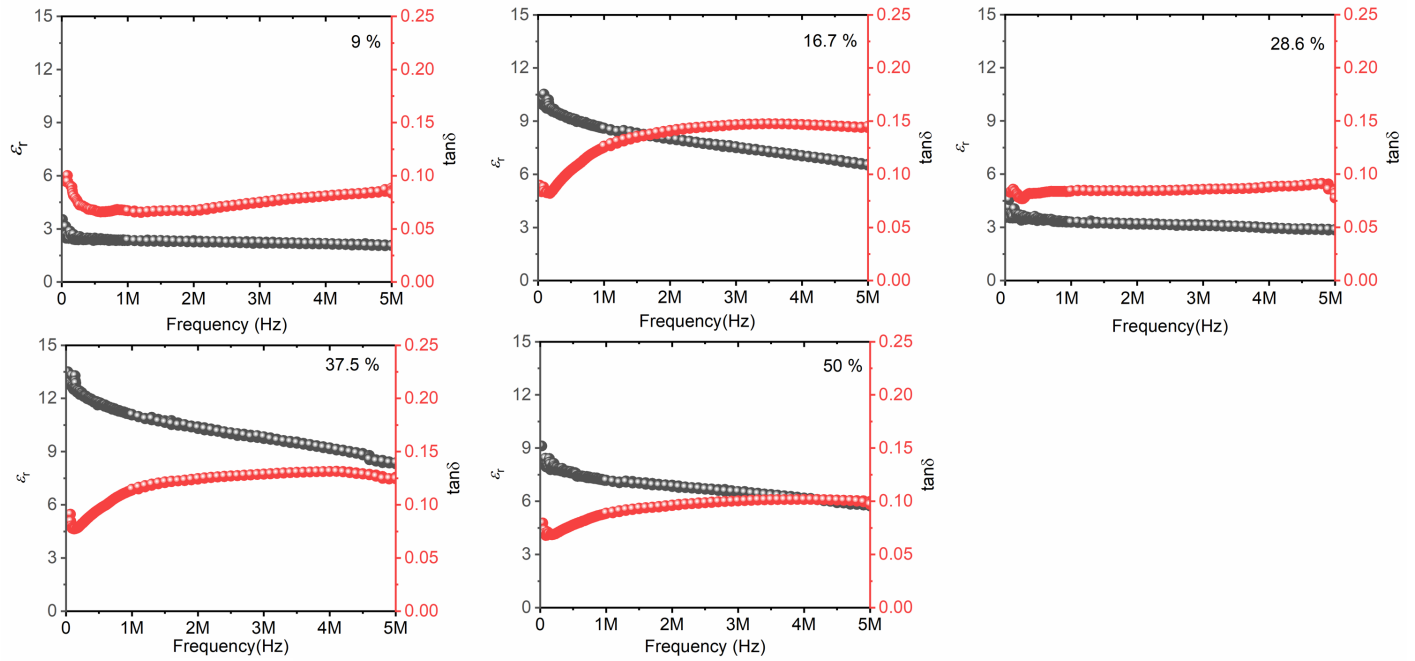


Figure 3. Relative permittivity (black symbols) and dielectric loss tangent (red symbols) as a function of frequency for PVDF/BCZT films containing 9–50 wt.% BCZT.

can be compared, the loops are narrow, nearly linear, and unsaturated. With increasing field the loop opens most for the 9 wt.% film, while the films with more ceramic stay comparatively slim over the field ranges reached. None of the loops saturates, so they are better described as lossy dielectric loops with weak hysteresis than as ferroelectric switching loops. Leakage current was not measured independently, so the conduction and polarization contributions to the loss cannot be separated.

The recoverable energy density was obtained from the discharge branch between the remanent polarization (P_r) and the maximum polarization ($P_{\max}$), and the stored energy density from the charging branch:

$$W_{\text{rec}} = \int_{P_r}^{P_{\max}} E \, dP, \quad (1)$$

$$W_{\text{stor}} = \int_0^{P_{\max}} E \, dP. \quad (2)$$

The energy-storage efficiency is

$$\eta = \frac{W_{\text{rec}}}{W_{\text{stor}}} \times 100\%, \quad (3)$$

where E is the applied electric field and P is the polarization. The energy density lost per cycle is $W_{\text{loss}} = W_{\text{stor}} - W_{\text{rec}}$. These are the usual definitions for charge–discharge P – E loops of dielectric energy-storage materials [2, 8].

The values of $P_{\max}$, W_{rec} , W_{stor} , W_{loss} , and η from the 100 kV cm^{−1} loops are listed in Table 2. Since the field is the same for all films, this is the table to use for the effect of BCZT content. $P_{\max}$ rises from 0.12 $\mu\text{C cm}^{-2}$ at 9 wt.% to 0.25 $\mu\text{C cm}^{-2}$ at 37.5 wt.% and falls back to 0.22 $\mu\text{C cm}^{-2}$ at 50 wt.%; W_{rec} follows the same course, from 0.0046 to 0.0106 J cm^{−3} and then 0.0085 J cm^{−3}. The efficiency stays between 79 and 83% up to 37.5 wt.% and drops to 70.2% at 50 wt.%, where W_{loss} is largest. The 37.5 wt.% film, which has the highest permittivity in Figure 3, therefore also gives the highest polarization and recoverable energy density at equal field.

The parameters from the highest-field loop of each film are given separately in Table 1. The field amplitudes of these loops range from 100 to 700 kV cm^{−1}, so the table shows what each film reached within its own measured range and is not a comparison at equal field. The 9 wt.% film has the largest $P_{\max}$ (0.97 $\mu\text{C cm}^{-2}$) and W_{rec} (0.145 J cm^{−3}), but it was also taken to the highest field, 700 kV cm^{−1}, and its efficiency there is only 33.7%. Among the maximum-field loops the 28.6 wt.% film has the highest efficiency, 73.9% at 300 kV cm^{−1}; at the same field the 37.5 wt.% film gives $W_{\text{rec}} = 0.091 \text{ J cm}^{-3}$ and $\eta = 69.5\%$. The highest field in Table 1 is not a breakdown strength, and no statistical breakdown analysis was done in this work. The same caution applies when energy-storage values from studies carried out at different fields and with different breakdown protocols are compared [6, 8, 10].

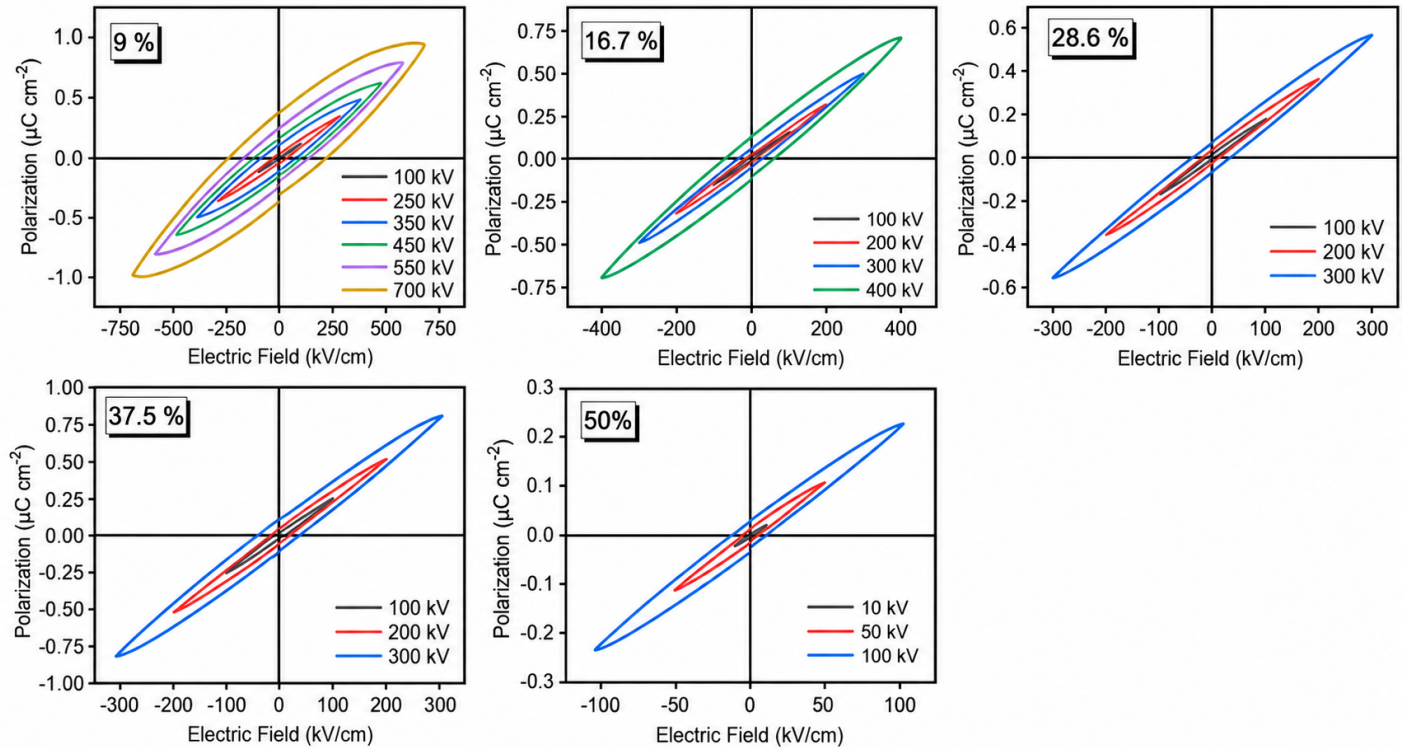


Figure 4. Polarization–electric-field loops of PVDF/BCZT films containing 9–50 wt.% BCZT.

Table 1. Polarization and energy-storage parameters obtained from the highest recorded P – E loop for each composition. The 50 wt.% film was not measured above 100 kV cm^{−1}; its values are therefore the same as in Table 2.

BCZT (wt.%)	Highest recorded field, $E_{\max}$ (kV cm ^{−1})	$P_{\max}$ (μC cm ^{−2})	W_{rec} (J cm ^{−3})	W_{stor} (J cm ^{−3})	W_{loss} (J cm ^{−3})	η (%)
9	700	0.97	0.145	0.430	0.285	33.7
16.7	400	0.70	0.104	0.168	0.064	61.9
28.6	300	0.58	0.068	0.092	0.024	73.9
37.5	300	0.80	0.091	0.131	0.040	69.5
50	100	0.22	0.0085	0.0121	0.0036	70.2

Table 2. Polarization and energy-storage parameters of PVDF/BCZT composite films evaluated at the common electric field of 100 kV cm^{−1}.

BCZT (wt.%)	$P_{\max}$ (μC cm ^{−2})	W_{rec} (J cm ^{−3})	W_{stor} (J cm ^{−3})	W_{loss} (J cm ^{−3})	η (%)
9	0.12	0.0046	0.0057	0.0011	80.7
16.7	0.17	0.0068	0.0082	0.0014	82.9
28.6	0.175	0.0072	0.0091	0.0019	79.1
37.5	0.25	0.0106	0.0132	0.0026	80.3
50	0.22	0.0085	0.0121	0.0036	70.2

4 Conclusion

PVDF/BCZT films with 9–50 wt.% BCZT were made by solution casting from solid-state-synthesized powder, and XRD shows that the perovskite BCZT phase is retained in the semi-crystalline polymer. The permittivity is frequency dependent and does not scale

simply with ceramic content: the 37.5 wt.% film has the highest value (about 11.5 falling to 8.2 at 5 MHz, $\tan \delta$ 0.08–0.13), whereas the 28.6 wt.% film lies well below its neighbors. At 100 kV cm^{−1} all loops are slim and unsaturated, and the 37.5 wt.% film again gives the largest $P_{\max}$ and W_{rec} with an efficiency of about 80%. At higher fields, the 9 wt.% film reaches $W_{\text{rec}} = 0.145$ J cm^{−3} at 700 kV cm^{−1} but with low efficiency, and the 28.6 wt.% film reaches 73.9% at 300 kV cm^{−1}; because the films were not driven to the same field, these numbers are not a ranking. Within this series the 37.5 wt.% composition gives the strongest dielectric and equal-field polarization response. Measurements on neat PVDF, microstructural characterization of filler dispersion, and breakdown testing under a common protocol are needed to explain the non-monotonic trend.

Data Availability Statement

Data will be made available on request.

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Conflicts of Interest

The authors declare no conflicts of interest.

AI Use Statement

The authors declare that ChatGPT-5 was used for language editing of the manuscript. The authors have carefully reviewed, revised, and verified the AI-assisted output and take full responsibility for the content of the manuscript.

Ethical Approval and Consent to Participate

Not applicable.

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