

Study on Energy Storage Performance of Dielectrics Based on PVDF/PMMA Blends and Multilayer Structures

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Abstract: To overcome the low energy density of polymer dielectrics, high-polarization poly(vinylidene fluoride) (PVDF) and high-breakdown-strength poly(methyl methacrylate) (PMMA) composites were fabricated via solution blending (B-PVDF/PMMA) and layered hot-pressing (L-PVDF/PMMA). FTIR analysis reveals that blending introduces steric hindrance that disorders polar crystalline domains, whereas the layered structure effectively preserves the highly crystalline β -phase. Benefiting from Maxwell-Wagner-Sillars interfacial polarization and the physical barrier effect of the PMMA layer, the layered film significantly suppresses conduction loss and retards electrical tree growth. It achieves an enhanced breakdown strength of 495 MV/m with a Weibull shape parameter of 13.41, outperforming the blended system (482 MV/m, shape parameter 8.29). Consequently, at 518 MV/m, the layered composite delivers a superior discharge energy density of 9.53 J/cm³ while maintaining a charge-discharge efficiency of 75%, providing an effective structural design strategy for high-performance dielectric energy storage.

1. Introduction

The demand for high-performance dielectric capacitors is urgent for advanced pulse power systems and flexible DC transmission networks, but their relatively low energy storage density has become a key bottleneck restricting the lightweight and miniaturization of electrification systems [1]. Polymer-based dielectrics are highly attractive; specifically, poly(vinylidene fluoride) (PVDF) offers a high dielectric constant but suffers from large dielectric loss, whereas poly(methyl methacrylate) (PMMA) exhibits high breakdown strength and low loss [2, 3]. Compositing PVDF with PMMA is a promising strategy to achieve synergistic energy storage optimization [4].

Current composite strategies primarily involve two structural approaches: Blend structures achieve functionality through high insulation polymers, but the improvement is limited due to micro defects caused by blending [5], multilayer structures enhance breakdown strength and energy density by redistributing internal electric fields [6,7]. However, systematic comparative studies on the structure-property relationships of hybrid and layered interfaces within the same material system remain lacking.

To address this, this study constructs blended and layered PVDF/PMMA films via solution blending and hot-pressing processes, respectively. We systematically compare their dielectric properties,

breakdown characteristics, and energy storage densities to reveal the regulatory mechanisms of different structures.

2. Experiment

2.1. Materials

PVDF used in this study was provided by Shanghai 3F New Materials Co., Ltd. PMMA was supplied by Macklin Biochemical Co., Ltd. N,N-Dimethylformamide (DMF) was purchased from China National Pharmaceutical Group Corporation.

2.2. Film Preparation

Preparation of blended films: For the blended films, PVDF (0.50 g) was dissolved in 10 ml of DMF and stirred at room temperature for 6 h. Subsequently, PMMA (0.50 g) was added to the solution, and the mixture was stirred for an additional 10 h to ensure complete dissolution and homogeneous mixing [8]. The resulting solution was cast onto a glass plate, and a wet film was prepared using a doctor blade. The wet film was then dried in an oven at 80°C for 10 h to obtain the PVDF/PMMA blended film (denoted as B-PVDF/PMMA). For the layered films, PVDF (1 g) was dissolved in 10 ml of DMF and stirred at room temperature for 12 h to obtain a PVDF solution, from which a PVDF single-layer film was prepared following the same casting and drying procedure described above. Similarly, PMMA (3 g) was dissolved in 10 ml of DMF and stirred at room temperature for 12 h to obtain a PMMA solution, which was used to fabricate a PMMA single-layer film. The PVDF and PMMA single-layer films with identical thickness were stacked together and placed in a flat vulcanizing machine at 120°C. The pressure was increased to 10 MPa and maintained for 20 min to produce the PVDF/PMMA layered film with a 1:1 thickness ratio (denoted as L-PVDF/PMMA). All film samples prepared as described above were controlled to a uniform thickness of approximately 10 μm .

3. Results and Discussion

3.1. FTIR Analysis

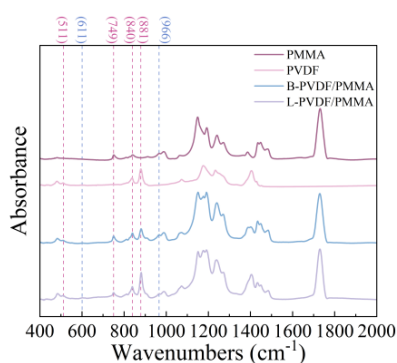


Fig. 1. FTIR of PVDF, PMMA and Their Composites.

By comparing the FTIR spectra of samples under different preparation processes (Figure 1), the distinct effects of the blended and layered structures were further investigated. In the pure PVDF spectrum, the strong absorption peaks at 840 cm^{-1} and 881 cm^{-1} confirm that it mainly exists in the form of the polar β -phase, which lays a solid structural foundation for obtaining a high dielectric response. For the blended sample, although the main characteristics of the β -phase are maintained, the peak shapes at 840 cm^{-1} and 881 cm^{-1} exhibit obvious broadening and intensity attenuation.

Concurrently, weak diffuse responses appear at 611 cm^{-1} and 966 cm^{-1} . This is attributed to the significant steric hindrance and dipole-dipole interference generated by the amorphous PMMA chains in the B-PVDF/PMMA, which limits the all-trans arrangement of PVDF molecular chains and leads to the disordering of polar crystalline domains^[9, 10].

In contrast, the layered structure exhibits a significant structural stability advantage. In the spectrum of the layered sample, the characteristic peaks at 840 cm^{-1} and 511 cm^{-1} still maintain extremely high sharpness and absorption intensity. The layered preparation process effectively avoids the interference of PMMA on PVDF through macroscopic phase separation, enabling the PVDF layer to maximally retain its original highly crystalline β -phase structure, thereby ensuring a higher polarization intensity of the material under an electric field.

3.2. Dielectric Properties Analysis

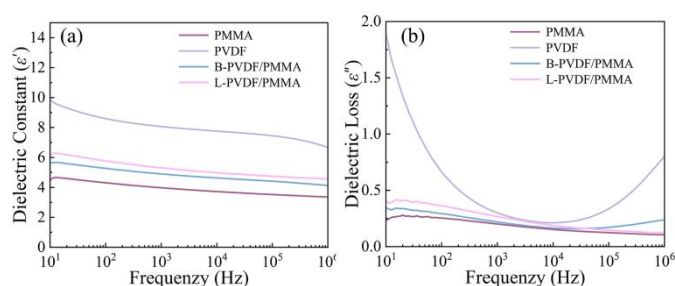


Fig. 2. Frequency dependent of (a) ϵ' and (b) ϵ'' of dielectric composite at room temperature.

To investigate the influence of different composite structures on the dielectric behavior of the materials, the dielectric constant (ϵ') and dielectric loss (ϵ'') of the samples were tested in the frequency range of 10^1 to 10^6 Hz. As shown in Figure 2a, pure PVDF exhibits the highest dielectric constant due to its intrinsic polar β -phase, while pure PMMA exhibits the lowest dielectric constant owing to its amorphous and weakly polar nature. Between the two composite materials, the dielectric constant of the layered structure is significantly higher than that of the blended structure across the entire tested frequency band. The layered preparation process avoids mutual interference between the components, enabling the PVDF layer to retain the β -phase, which provides a polarization contribution to the layered structure. In the low-frequency region, the dielectric constant of the layered structure presents an enhancement phenomenon attributed to the Maxwell-Wagner-Sillars (MWS) interfacial polarization effect; the physical interface between PVDF and PMMA causes free charges to accumulate, thereby increasing the overall dielectric constant.

As shown in Figure 2b, in terms of dielectric loss, pure PVDF exhibits extremely high loss in both the low-frequency and high-frequency regions, restricting its energy storage applications. Both B-PVDF/PMMA and L-PVDF/PMMA suppress the loss, but via different mechanisms. The dielectric loss of the blended structure remains stable and extremely low across the entire frequency band. This is because the intercalation of PMMA molecular chains disrupts the long-range order of PVDF crystalline domains; the change of polar units reduces the dipole-flipping resistance and restricts the movement of polymer chain segments as well as the migration of charge carriers, thereby suppressing conduction and relaxation losses.

The loss curve of the layered structure confirms its interfacial coupling mechanism. At low frequencies, the loss of the layered sample is slightly higher than that of the blended sample, which is a manifestation of energy dissipation from interfacial polarization. As the frequency increases, the loss of the layered sample decreases rapidly. In the high-frequency region, the loss falls below that of the blend and approaches pure PMMA, indicating that the PMMA layer blocks carrier transport pathways and shields the high-frequency relaxation loss of the PVDF layer.

3.3. Electrical Breakdown Performance Analysis

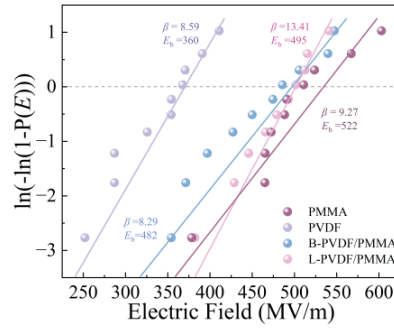


Fig. 3. Weibull distribution of breakdown strength for dielectric composites at room temperature.

To evaluate the voltage endurance and insulation reliability of composite materials in practical energy storage applications, breakdown tests were conducted on films under different preparation processes, and the experimental data were statistically analyzed using the Weibull distribution model. Its mathematical expression is:

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

Here, $P(E)$ is the cumulative probability of breakdown, E is the experimentally measured breakdown electric field, E_b is the characteristic breakdown strength (the electric field value at a cumulative breakdown probability of 63.2%), and β is the shape parameter characterizing the reliability of the film. A larger β value indicates fewer internal defects in the material and a correspondingly higher breakdown strength. The Weibull distribution fitting results for each sample are shown in Figure 3. Pure PVDF exhibits the lowest E_b of only 360 MV/m and a β value of 8.59. As a polar polymer, it suffers from high internal conduction loss and is prone to generating Joule heat under strong electric fields, which leads to premature breakdown. Relying on its excellent intrinsic insulation performance, pure PMMA exhibits a high breakdown strength of 522 MV/m.

After compounding PMMA with PVDF, the E_b of both the blended and layered structures is significantly enhanced compared to pure PVDF. The E_b of B-PVDF/PMMA increases to 482 MV/m because the PMMA exhibits excellent insulation properties. However, the β value of the blended sample decreases to 8.29, displaying the broadest dispersion of breakdown data. Combined with the FTIR analysis, although blending achieves fully homogeneous blend, it introduces more microstructural defects and free volumes. Under high electric fields, these easily act as electric field distortion points, reducing breakdown stability and macroscopic reliability.

In contrast, L-PVDF/PMMA exhibits a higher characteristic breakdown strength (495 MV/m) and a β value up to 13.41, far exceeding the other samples. This significant enhancement is primarily attributed to the redistribution of the electric field within the bilayer structure. Consequently, the PMMA layer, which possesses a lower dielectric constant, inherently bears a substantially higher proportion of the electric field. Since pure PMMA exhibits excellent intrinsic insulation performance, it safely accommodates this intensified field, thereby effectively shielding the high-permittivity PVDF layer from premature failure. The layering process preserves the integrity of PVDF and avoids the local phase separation and defects associated with blending, granting the film high structural consistency and resulting in an advantageous β value [11].

3.4. Analysis of P-E Loop Characteristics

To evaluate the polarization characteristics and energy loss mechanisms of the composite films in

energy storage applications, the polarization-electric field (P - E) hysteresis loops of each sample under maximum electric fields were tested, and the results are shown in Figure 4. From the trends of the hysteresis loops (Figure 4a), pure PVDF exhibits a broad typical ferroelectric loop and approaches its breakdown limit at 350 MV/m. Although its maximum polarization (P_m) is relatively high, its remnant polarization (P_r) is large, originating from the difficult flipping of large-sized polar β domains and leakage current. Conversely, pure PMMA displays good linear dielectric characteristics with a narrow and elongated loop, but its P_m is restricted by its weak polarity.

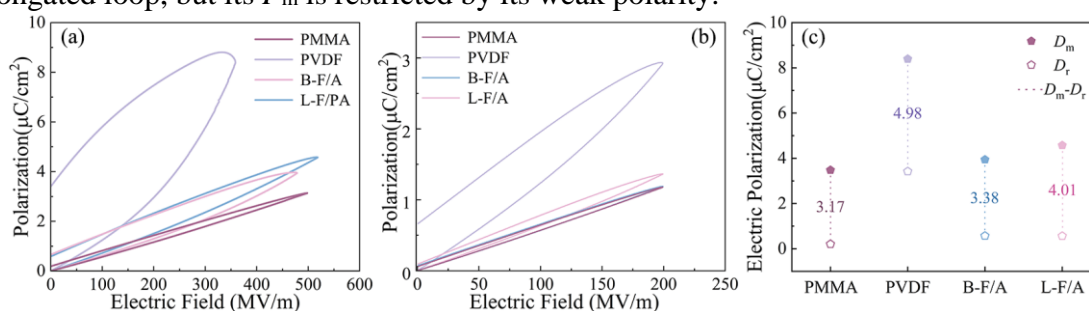


Fig. 4. Comparison of polarization characteristics between films: (a) comparison of P - E curves under maximum electric field conditions, (b) comparison of P - E curves for each film at 350 MV/m, (c) comparison of P_m and P_r values for each film under the maximum electric field.

Under the same electric field (200 MV/m, Figure 4b), both the B-PVDF/PMMA and L-PVDF/PMMA composite films transform the broad hysteresis loop of pure PVDF into quasi-linear loops, indicating that the introduction of PMMA suppresses ferroelectric flipping and conduction losses. Moreover, the polarization intensity of the layered structure is slightly higher than that of the blended structure. This is because the layered configuration possesses interfacial polarization, and the layering process preserves the highly crystalline polar β -phase of PVDF, providing a stronger polarization response.

The polarization characteristics of the composite films at their breakdown limits are shown in Figure 4c. The key parameter determining the releasable energy density of dielectrics is $P_m - P_r$. In the blended structure, the spatial confinement of PVDF by PMMA chain segments suppresses P_r , but the maximum polarization is affected, resulting in a $P_m - P_r$ of $3.38 \mu\text{C}/\text{cm}^2$. The layered structure exhibits excellent polarization performance; the interfacial blocking effect increases the breakdown field strength, allowing P_m to be fully released. Simultaneously, the PMMA insulating layer cuts off leakage current pathways and reduces dielectric loss, keeping P_r low. Consequently, $P_m - P_r$ reaches $4.01 \mu\text{C}/\text{cm}^2$, the highest value among the composite systems.

3.5. Energy Storage Performance Analysis

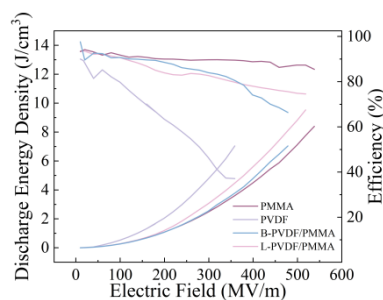


Fig. 5. Discharge energy density and efficiency of dielectric composite at room temperature.

The practical application potential of dielectric materials is jointly determined by the releasable energy density (U_e) and charge-discharge efficiency (η), as shown in Figure 5. The figure displays the

curves of energy density and charge-discharge efficiency for each sample. Although the U_e of pure PVDF increases rapidly under low electric fields, restricted by ferroelectric hysteresis loss and early breakdown, its maximum discharge energy density is only 7.04 J/cm^3 , and its efficiency deteriorates to 40% under high electric fields. Pure PMMA maintains an efficiency of around 90% across the entire electric field range, but its U_e is relatively low due to its amorphous and non-polar structure.

After compounding PVDF with PMMA, the comprehensive energy storage properties are significantly optimized. At its maximum tolerant electric field (478 MV/m), the B-PVDF/PMMA achieves an energy density of approximately 7.04 J/cm^3 and a charge-discharge efficiency of about 66%. In conjunction with the previous analysis, the strong interactions introduced by the mixture promote the β -phase transition. While this reduces remnant polarization, it disrupts the long-range order of the crystals, sacrificing partial polarization intensity. Furthermore, the internal inhomogeneity of the blend restricts the breakdown field strength, limiting the upper bound of the energy storage density. In comparison, the L-PVDF/PMMA exhibits the optimal comprehensive energy storage performance. Under the highest applied electric field (518 MV/m), its maximum energy density reaches approximately 9.53 J/cm^3 , while the discharge efficiency is maintained at 75%. This excellent performance results from the synergistic action of multiple physical mechanisms. The layering process preserves the long-range ordered structure of the highly pure β -phase within the PVDF layer; the Maxwell-Wagner-Sillars (MWS) interfacial polarization effect contributes an additional interfacial polarization increment; and the PMMA layer cuts off conduction pathways and retards the growth of electrical trees, ensuring that polarization energy is stored and released under high electric fields.

4. Conclusion

This study investigates PVDF/PMMA composite films prepared via solution blending and layered hot-pressing. The layered structure effectively preserves the highly crystalline β -phase of PVDF and utilizes the PMMA insulating barrier to suppress dielectric loss and electrical tree growth. Consequently, the layered film exhibits an enhanced breakdown strength of 495 MV/m with a high Weibull shape parameter of 13.41. At 518 MV/m, it achieves a superior discharge energy density of 9.53 J/cm^3 and 75% efficiency. This macroscopic layered design successfully decouples high polarization and insulation, offering an effective structural engineering strategy for high-performance dielectric energy storage capacitors.

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