The effect of multilayered film structure on the dielectric properties of composites films based on P(VDF-HFP)/Ni(OH)$_2$

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ABSTRACT

High dielectric constant ceramics fillers are widely used as fillers in polymer matrix to prepare high performance dielectric composites. Homogeneous filler distribution in these composites films is found to be quite difficult to achieve balance between high dielectric constant and high breakdown strength. Herein, multilayer structured composites films containing nickelous hydroxide (Ni(OH)$_2$) as fillers, with different multilayered structures were designed and prepared, including 2-5 layers structure with various filler distribution. The effects of multilayer structure on the dielectric performance are explored by keeping the overall filler content constant. Combined with computer simulation, it is suggested that the variation in filler distribution in these films can effectively redistribute electric field intensity. Meanwhile, the dielectric constant and breakdown strength of the overall composites can be adjusted by changing the volume ratio between high filler content layer and low filler content layer. It is noted that at least 1/3 of the overall film volume should be occupied by a high breakdown strength layer to keep rather high overall breakdown strength. Moreover, high dielectric constant layer should be the outer layers to achieve overall high dielectric constant. Among all the layered structures investigated, the maximum energy density of 6.03 J/cm$^3$ is obtained for film with a 3-layer nonsequential arrangement structure, which is 68% higher than single layer film with identical composition. This study provides some reference value for the preparation of multilayered dielectric polymer composites films for energy storage applications.

GRAPHICAL ABSTRACT

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Introduction

High energy storage density ($U_e$) dielectric capacitor materials with high dielectric constant ($\varepsilon_r$), high breakdown strength ($E_b$) and low dielectric loss are of great significance for the preparation of electrical components. Traditional ceramic dielectrics have great advantages in terms of their high dielectric constant. Such as barium titanate (BaTiO$_3$, $\varepsilon_r \sim 1500$–4600 [1,2]), lead zirconate titanate (PZT, $\varepsilon_r \sim 200$–800 [3]). Polymer-based dielectric materials exhibit a high dielectric breakdown strength, excellent flexibility and low density comparing with...
ceramics dielectrics. But the energy storage density was limited by low dielectric constant (generally \(e_r < 5\) at 1000 Hz [4–6]) of neat polymer for application. At present, poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene (P(VDF-TrFE)), hexafluoropropylene (P(VDF-HFP)) are widely studied polymer dielectric materials because of their high dielectric constant (8–12 at 1000 Hz) [7]. To enhance the dielectric performance of polymer dielectrics, ceramic/polymer composites have been studied to obtain high dielectric constant [8–14]. The introduction of high dielectric constant ceramic materials does contribute to the dielectric properties of these composites. For instance, Zhang et al. [15] introduced TiO\(_2\) nanofibers embedded with BaTiO\(_3\) nanoparticles into P(VDF-HFP) polymer matrix, the energy storage density was enhanced to \(\sim 31.2 \text{ J/cm}^3\) with a \(E_b\) of \(\sim 800 \text{ kV/mm}\).

Nevertheless, high dielectric constant composites are generally accompanied by more leakage current and loss with high filler content, causing decreased breakdown strength [18–24]. In general, the electric field near high dielectric constant fillers is much higher than that of the other part of polymer matrix. Such strong local electric field could cause higher probability of breakdown, especially for rather high filler content. The \(U_e\) of dielectrics could be expressed by formula \(U_e = \int E \text{d}D\), in addition, it can be calculated by formula \(U_e = 1/2e_r\varepsilon_0E_b^2\) for non-ferroelectric linear dielectrics. Obviously, the breakdown strength \(E\) and dielectric constant \((e_r)\) are positively correlated with \(U_e\). Consequently, it is important to enhance the dielectric constant of composites, while avoiding decrease in breakdown strength. Therefore, structuring multilayer film is a simple and effective method to achieve this goal, where high filler content layers provide high dielectric constant and low filler content layers avoid increasing leakage current. At present, most studies for multilayer composites films usually have a sandwich structure with a high dielectric constant layer (HD layer) as the outer layer, and a high breakdown strength layer (HB layer) as the inner layer. Some reports on multilayer structure are listed in Table 1. It is thought that the introduction of a low dielectric and high breakdown layer in these multilayer films can unevenly distribute electric field in these materials, reducing the internal field strength in the HD layer and improving the overall breakdown strength and energy storage density of these composites.

From Ref. [29,31,32], it is reported that each layer in multilayer structure film formed by adjusting filler content can contribute their advantages to the overall film, resulting in improved both dielectric constant and breakdown strength. The dielectric constant and breakdown strength can both be adjusted in a balanced range to obtain the maximum energy storage density. Comparing with single layer composites, multilayered structure can improve the energy density by 100%. This effect can also be achieved by different fillers for each layer [33,34].

However, multilayer structures can be designed differently, and there are few studies on the properties of non-sandwich multilayer structured films. It is believed that multilayer films with different structures could have different effects on the dielectric properties, issues such as the number of layers and the location of specific layers should be further investigated to further understand the mechanism. Herein, nine different structures were designed to fabricate multilayer composite films. In addition to the common sandwich structures, asymmetric and alternating multilayer films were also designed to explore their dielectric properties.

\(\text{Ni(OH)}_2\) has often been used as the electrode materials for supercapacitors. Our group has recently used this type of materials as filler for dielectric polymer composites [35–37]. Comparing with other dielectric filler such as BaTiO\(_3\), Ni(OH)\(_2\) can be dispersed homogeneously in PVDF matrix without any surface modification due to their strong interaction with polymer matrix. Therefore, it is more likely to maintain low dielectric loss and prohibit leakage current with rather high content of Ni(OH)\(_2\). Herein, hexagonal-like structured Ni(OH)\(_2\) flakes were prepared by hydrothermal method and

Table 1. Literature reports on dielectric multilayer films.

| Samples                  | Structure       | Variable                  | Filler                     |
|--------------------------|-----------------|---------------------------|----------------------------|
| BaTiO\(_3)/PVDF [25]     |                 | Thickness of HD layer      | Identical                  |
| BNNS/PVDF/PVDF [26]      |                 | Filler content in HD layer | Multiple                   |
| PVDF/P(VDF-TrFE-CTFE) [27]|                 | Thickness of HD layer      | None                       |
| BaTiO\(_3)/PVDF [28]     |                 | Filler content in HD and HB layer | Various morphologies of the same material |
| NBBT/P(VDF-HFP) [29]     |                 | Thickness of HD and HB layer | Identical                  |
| BaTiO\(_3)/PVDF-HFP) [30]|                 | Thickness of HD layer      | Identical                  |
| BaTiO\(_3)/PVDF [31]     |                 | Filler content in HD layer | Identical                  |
| BaTiO\(_3)/PVDF [32]     |                 | Filler content in HD layer | Identical                  |
| TiO\(_2\)-Ba\(_x\)TiO\(_3\)/PVDF [33]| | Filler content in HB layer | Multiple                   |
| BZT-BCT/Fe\(_3\)O\(_4\)@BNNS/PVDF [34]| | Filler content in HB layer | Multiple                   |
added into P(VDF-HFP) matrix to prepare single-layer and multilayer composites films. The effects of the number of layers and location of a specific layer on the final dielectric properties of the overall films have been studied. The mechanism responsible for observed effect is discussed.

**Experimental section**

**Materials**

$N$, $N$-dimethylformamide (DMF), ammonia water ($\text{NH}_3\cdot\text{H}_2\text{O}, 25\%$) and nickel chloride hexahydrate ($\text{NiCl}_2\cdot\text{H}_2\text{O}$) were purchased from Kelong Co., Chengdu, China. P(VDF-HFP) was purchased from Sigma-Aldrich ($M_w \sim 400,000$).

**Preparation of nickel hydroxide nano flakes**

Nickel hydroxide nano flakes were synthesized by hydrothermal method. 2.314 g $\text{NiCl}_2\cdot\text{H}_2\text{O}$ was firstly dissolved in 200 ml deionized water with slow stirring. Gradually, 6 ml $\text{NH}_3\cdot\text{H}_2\text{O}$ (25%) was dripped in above solution. The mixture was then transferred into a 300 ml stainless steel autoclave with a Teflon liner and subsequently annealed at 220 °C for 6 h. Finally, the resulting product was collected by filtering and washed with deionized water and ethanol several times, then, dried under 60 °C for 24 h in vacuum.

**Fabrication of Ni(OH)$_2$/P(VDF-HFP) single-layer and multilayer film**

For the fabrication of Ni(OH)$_2$/P(VDF-HFP) single-layer composite film, desired amount of P(VDF-HFP) particles were dissolved in DMF with stirring under 60 °C for 1 h. Then, certain amount of Ni(OH)$_2$ nano flakes [10 wt% (4.4 vol%), 30 wt% (15.0 vol%) and 50 wt% (29.3 vol%)] were dispersed in the solution by ultrasonication for 3 h and subsequently stirred for 24 h. The resulting uniform suspension was dropped onto a clean glass substrate and spread by an adjustable scraper, followed by drying at 60 °C in vacuum for 12 h. Finally, the single-layer film was pressed at 200 °C for 30 min under a pressure of 10 MPa obtaining the final composites film with a thickness around 20 μm. Ni(OH)$_2$/P(VDF-HFP) multilayer films were fabricated layer by layer with the same spread process. Herein, adjusting the thickness of each layer by changing the height of scraper, and keep the overall thickness between 20 and 30 μm. To ensure the consistency of the overall filler content in multilayer films, the thickness ratio of each layer was controlled. A schematic diagram of the specimens preparation process is shown in Figure 1. Finally, the films were annealed by hot pressing at 200 °C, 10 MPa for 30 min. These multilayer films were arranged in different orders: 10 wt%–50 wt% (marked in L2), 50 wt%–10 wt%–50 wt% (L3), 10 wt%–30 wt%–50 wt% (L3a), 10 wt%–50 wt%–10 wt%–50 wt% (L4), 10 wt%–50 wt%–10 wt% (L3r), 50 wt%–10 wt%–30 wt% (L3s), 50 wt%–30 wt%–10 wt%–30 wt%–50 wt% (L5), 10 wt%–30 wt%–50 wt%–30 wt%–10 wt% (L5r) and 50 wt%–40 wt%–30 wt%–20 wt%–10 wt% (L5a).

**Characterization**

The powder X-ray diffraction (XRD) measurement were carried out under a Philips X’Pert pro MPD X-ray detector with Cu Kα radiation ($\lambda = 0.154$...
Characterization of synthesized Ni(OH)₂

Ni(OH)₂ prepared by hydrothermal method could be easily transformed into different morphologies by adjusting reaction conditions. Under certain temperature and pressure conditions, Ni(OH)₂ appears as specific crystal form and morphology through recrystallization. Figure 2(a) shows the SEM image of synthesized Ni(OH)₂. It can be seen that Ni(OH)₂ presents a homogeneous hexagonal flake structure with diameter about 140 nm. Obviously, the diffraction peaks at 2θ = 18.8°, 33.1°, 38.2°, 51.8°, 59.1° and 62.4° correspond to (001), (100), (101), (102), (110) and (111) crystal planes of β-Ni(OH)₂ (JCPDS Card No. 14-117), respectively, as shown in Figure 2(b). TGA curve shows that the decomposition temperature of synthesized Ni(OH)₂ is 280 °C, the final products are nickel oxide (NiO) and water. FT-IR spectra of the synthesized Ni(OH)₂ is shown in Figure 2(d). The spectrum of synthesized Ni(OH)₂ exhibits a absorption peak at 3641 cm⁻¹, which is assigned to the stretching of O-H without hydrogen bonds, the absorption peak near 460 cm⁻¹ is related to the lattice vibration of Ni-O, and the absorption peaks of stretching and bending vibration for the absorbed water are 3428.4 cm⁻¹ and 1618.9 cm⁻¹.

Characterization of Ni(OH)₂/P(VDF-HFP) composites

The cross sectional surface morphologies of 10 wt%, 30 wt%, 50 wt% Ni(OH)₂/P(VDF-HFP) and L3 composites films are shown in Figure 3(a–d), respectively. Ni(OH)₂ nanoflakes can be well dispersed in P(VDF-HFP) matrix without any surface modification due to the strong interaction between filler and matrix. The thickness of each layer in the multilayer films is consistent with that calculated during preparation, where the ratio is approximately 1:1 in L2; 1:2:1 in L3, L3r;
Figure 3. SEM images of Ni(OH)$_2$/P(VDF-HFP) composites films (a) 10 wt%, (b) 30 wt%, (c) 50 wt% and (d) L3.

Figure 4. (a) FT-IR and (b) XRD spectra of single-layer composites with various Ni(OH)$_2$ contents, (c) FT-IR spectra of neat Ni(OH)$_2$ and 10 wt% Ni(OH)$_2$/P(VDF-HFP) composites at 3640 cm$^{-1}$. (d) Schematic diagram of hydrogen bond structure between Ni(OH)$_2$ and P(VDF-HFP).
1:1:1 in L3a, L3s; 1:1:2:1 in L5, L5r and 1:1:1:1:1 in L5a, respectively. Finally, the average content of Ni(OH)$_2$ in these multilayer films was kept at 30 wt%. In addition, the interfaces between layer and layer are distinct as shown in Figure 3(d).

Figure 4(a) shows the FT-IR spectra of single-layer composites with varied Ni(OH)$_2$ contents. These samples exhibit absorption bands at wave-numbers of 766, 795, 854 and 974 cm$^{-1}$, which are characteristics of $\alpha$-crystalline P(VDF-HFP). This demonstrates that the matrix mainly exhibits $\alpha$-form crystals. In addition, two weak absorption bands are observed at 840 and 1275 cm$^{-1}$, attributing to the $\beta$-crystalline form. This indicates the presence of small amount of $\beta$-crystalline P(VDF-HFP). Furthermore, the relative content of $\beta$-crystalline phase can be calculated according to Lambert-Beer law as follows:

$$F(\beta) = \frac{A_\beta}{(K_a/A_a + K_\beta/A_\beta)}$$

Where $F(\beta)$ is the relative content of $\beta$-crystalline phase, $A_a$ and $A_\beta$ are absorbance strength at 766 cm$^{-1}$ and 840 cm$^{-1}$, $K_a$ and $K_\beta$ are absorbance index at 766 cm$^{-1}$ and 840 cm$^{-1}$, which is 6.1 × $10^4$ cm$^2$/mol and 7.7 × $10^4$ cm$^2$/mol, respectively. It can be obtained by calculating that the relative content of $\beta$-crystalline in 0 wt%, 10 wt%, 30 wt% and 50 wt% filler content samples is 0.1233, 0.1379, 0.1383 and 0.1298, respectively.

Figure 4(b) shows the XRD spectra of these single-layer composites. Neat P(VDF-HFP) exhibits characteristic peaks at 20 = 20.8° and 26.7°, attributing to the diffractions of (110) and (021) crystal surfaces of $\alpha$-crystalline P(VDF-HFP). However, it is difficult to recognize the $\beta$-phase from $\alpha$ phase because they have a common peak around 20°. The samples with high filler content exhibit obvious peaks which are assigned to Ni(OH)$_2$ fillers because of their high crystallinity. However, it does not induce much change in P(VDF-HFP) crystal form or crystallinity.

In addition, as shown in Figure 4(c), the FT-IR spectra of neat Ni(OH)$_2$ and 10 wt% Ni(OH)$_2$/P(VDF-HFP) showed that the -OH absorption peak of Ni(OH)$_2$ at 3640 cm$^{-1}$ is redshifted, which shows the formation of hydrogen bonds. The schematic diagram of hydrogen bond structure between Ni(OH)$_2$ and P(VDF-HFP) is shown in Figure 4(d). The -F on the molecular chain of P(VDF-HFP) can form hydrogen bonds with the -OH that arrange vertically in Ni(OH)$_2$ crystals.

Characterization of dielectric properties

Several groups of single-layer composites films with different Ni(OH)$_2$ content (5 wt%–50 wt%) have been prepared and their dielectric properties have been characterized as shown in Figure 5. The frequency dependence of dielectric constant and loss for single-layer neat polymer and composites films at room temperature are shown in Figure 5(a). Obviously, the dielectric constant of these

![Figure 5](image.png)

**Figure 5.** (a) Frequency dependence of dielectric constant and dielectric loss for neat P(VDF-HFP) and single-layer composites with various Ni(OH)$_2$ contents. (b) Weibull distribution of breakdown strength, (c) D-E loops, (d) maximum energy density and energy efficiency at 200 kV/mm with various Ni(OH)$_2$. 
composites presents an uptrend with increasing Ni(OH)\textsubscript{2} content in the frequency range of 40-10\textsuperscript{5} Hz. This is attributed to the interface polarization between Ni(OH)\textsubscript{2} fillers and polymer matrix. Pure P(VDF-HFP) matrix exhibits a dielectric constant of 10.9 at 10\textsuperscript{3} Hz, and 50 wt% Ni(OH)\textsubscript{2}/P(VDF-HFP) composites illustrates a value of 17.6 which is around 60% increase. Meanwhile, the dielectric loss of composites increases slightly with increasing filler content. The dielectric loss of neat polymer and these composites is 0.049 (10\textsuperscript{3} Hz) and ~0.06 (10\textsuperscript{4} Hz), respectively. Furthermore, the dielectric loss at high frequency (>10\textsuperscript{5} Hz) is higher than that at low frequency (10\textsuperscript{3}-10\textsuperscript{4} Hz) due to the generation of relaxation phenomena resulting from that the dipole could not keep up with the change of external electric field direction under high frequency.

The breakdown strength of films was measured by a withstand voltage tester (Changjiang CJ2671S, China). The films with thickness of ~20 μm are placed between a special copper needle electrode and a sheet electrode, then, completely immersed in high voltage silicone oil. The DC current is applied between the electrodes, and the boost rate is about 100 V/s. The characteristic breakdown strength of single-layer composites is calculated with following Weibull distribution function:

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

Where \( P(E) \) is the cumulative probability of breakdown, and \( P_i = \frac{i-0.44}{n+0.2} \times 100\% \), \( i = 1, 2, 3 \ldots \text{...} \text{...} n \), \( E_i \) is measured breakdown strength that arranged from low to high, \( E_b \) is characteristic breakdown strength at the probability of 63% for materials to breakdown, and \( \beta \) is the Weibull modulus related to the linear regressive fit of the distribution. Therefore, \( E_b \) can be calculated by converting the function to:

\[
\log[-\ln(1-P(E))] = \beta \log E_i - \beta \log E_b
\]

And the results are shown in Figure 5(b). The \( E_b \) of pure polymer is ~ 260 kV/mm, and the \( E_b \) of single layer composites appears a tendency of increase first and then decrease with increasing filler content. It reaches a maximum value of 300 kV/mm when the content of Ni(OH)\textsubscript{2} is 10 wt%. A certain content of Ni(OH)\textsubscript{2} nano-flakes could play a role in blocking the current breakdown by hindering the growth of electrical tree under applied external electric field [38]. But excessive filler content causes significant increase in local electric field, resulting in higher probability to breakdown. Typical D–E loops of the pure P(VDF–HFP) and Ni(OH)\textsubscript{2}/P(VDF-HFP) composites for various Ni(OH)\textsubscript{2} loadings are shown in Figure 5(c). With increasing Ni(OH)\textsubscript{2} loading, electric displacement increased notably under the same electric field. The maximum displacement of pure P(VDF–HFP) was 2.57 μC/cm\textsuperscript{2} under an electric field of 200 kV/mm and increased to 5.14 μC/cm\textsuperscript{2} for the composite with 50 wt% Ni(OH)\textsubscript{2} under the same electric field. The increased displacement is attributable to the increase in relative permittivity of the composites. The energy storage density and energy efficiency of the samples are shown in Figure 5(d). 10 wt% Ni(OH)\textsubscript{2}/P(VDF-HFP) composites illustrates the highest energy storage density of 5.01 J/cm\textsuperscript{3}, which is 66% higher than that at 3.03 J/cm\textsuperscript{3} of neat P(VDF-HFP) because of its high breakdown strength. In addition, 30 wt% Ni(OH)\textsubscript{2}/P(VDF-HFP) and 50 wt% Ni(OH)\textsubscript{2}/P(VDF-HFP) illustrate energy density of 3.59 J/cm\textsuperscript{3} and 2.75 J/cm\textsuperscript{3}, respectively. It can also be seen that the energy efficiency decreases with increasing filler content, from 0.71 for neat P(VDF-HFP) to 0.43 for 50 wt% Ni(OH)\textsubscript{2}/P(VDF-HFP).

To investigate the effect of film structure on the final dielectric properties of these films, different multilayered films were prepared with constant Ni(OH)\textsubscript{2} content (30 wt%). The schematic diagrams of the structure of each sample are shown in Figure 6(a). For multilayer films and single-layer control samples, the frequency dependence of dielectric constant and loss analysis at room temperature are illustrated in Figure 6(b). In these 10 samples, the average content of Ni(OH)\textsubscript{2} are kept at 30 wt%. The dielectric constant are different because of their difference in film structure. The dielectric constant of multilayer films where the high filler content layer is the outer layer and the low content layer is the inner layer (L3 and L5) are higher than that of samples with opposite structure (L3r and L5r) at 10\textsuperscript{3} Hz. And the 5-layer structure composites films with a smaller concentration gradient (L5 and L5r) also illustrate higher dielectric constant than 3-layer structure films with a larger concentration gradient (L3 and L3r) at 10\textsuperscript{5} Hz. As a result of the difference in Ni(OH)\textsubscript{2} content in different layers, the interface polarization density between Ni(OH)\textsubscript{2} and P(VDF-HFP) matrix also appear for an uneven distribution. It is speculated that this phenomenon is caused by the distribution of interfacial polarization between fillers and polymer matrix in the multilayer structure films. In addition, the specimens with sequential arrangement structure (L2 and L3a) are asymmetrical structures and their dielectric constant is slightly lower than that of samples with sandwich structure (L3 and L5). It is thought that a symmetrical sandwich structure is more conductive for an electrode plate to store charge because of symmetrical polarization distribution. Moreover, the ability of an electrode
plate to store charge through polarization is stronger when the HD layer is close to the electrode plate. This agrees with some observations reported in Refs. [28,29,32,33,39,40].

The Weibull distribution of breakdown strength and characteristic breakdown strength of these 10 samples are listed in Figure 6(c,d). Results illustrate that the breakdown strength of multilayer structure samples is higher than that of single layer film in varying degrees because of the introduction of HB layer (low fillers content layer). Among them, 3-layer sandwich structure samples (L3 and L3r) and asymmetrical structure samples (L2, L3a, L3s and L4) demonstrate an obviously higher breakdown field distribution than that of the L1. However, the breakdown strength of 5-layer films (L5, L5r and L5a) is only similar to that of L1. It is found that the breakdown strength of samples is related to the proportion of HB layer in these films. As shown in Figure 7, the proportion of HB layer is 0 in sample L1; 0.2 in sample L5a; 0.33 in sample L3a, L3s, L5, L5r; 0.5 in sample L2, L3, L3r, L4 and 1.0 in 10 wt% Ni(OH)2 single-layer film. With increasing proportion of HB layer, the breakdown strength of samples shows an upward trend. In conclusion, at least 1/3 of the overall film volume should be occupied by the high breakdown strength layer to maintain a high overall breakdown strength, and for a HB layer content of 50%, the breakdown strength of multilayer films has almost reached that of the pure HB layer.

At last, three typical thin films were selected for D–E loop test. The energy storage density and energy efficiency of sample L3, L3s and L5 are shown in Figure 8. It is seen that there are only small differences in the electric displacement between the three studied films. Sample L5 shows the largest displacement among the three films under the same electric field. Sample L3s shows the highest energy storage density of 6.03 J/cm³.
because of its high breakdown strength. Sample L3 and L5 demonstrate 5.53 J/cm³ and 4.56 J/cm³, respectively. All of these are higher than that of 30 wt% Ni(OH)₂/P(VDF-HFP) single layer film. It is also interesting to note is that the energy efficiency of these three multilayer films is higher than single layer film, achieving 0.7, 0.68 and 0.6, respectively.

**Computer simulation**

To explore the mechanism for the influence of multilayer structures on final performance, the electric field is simulated by computer. The dielectric constant of single-layer film is set to 20 as shown in Figure 9(a), which represents the sample L1; Figure 9(b) represents sample L2, which the dielectric constant of the upper layer is set to 10, and the lower layer is set to 30. And so on, Figure 9(c–j) correspond to L3, L3r, L3a, L3s, L4, L5, L5r and L5a, respectively. Then, these 10 samples with equal thickness are placed between two electrodes with the same potential, and the distribution of electric field intensity is simulated as shown in Figure 9. Assuming that each layer is homogeneous, simulation displays that the electric field intensity is uniform in the single-layer film, it also indicates that the distribution of polarization...
inside the material is uniform. Nevertheless, it is uneven for the distribution of electric field intensity in the multilayer structure films resulting from the inhomogeneous polarization. And the dielectric field intensity inside the high filler content layers is weaker than that inside the low filler content layers, due to the stronger polarization counteract the effect of the external electric field.

The multilayer structure films could be regarded as several capacitors connected in series, thus, the local electric field of each layer could be obtained as follows for the 3-layer sandwich structured films [34,41,42]:

$$E_1 = \frac{V}{2d_1 + \frac{d_1}{d_2}}$$  \hspace{1cm} (1)
$$E_2 = \frac{V}{d_2 + \frac{2d_1}{d_1}}$$  \hspace{1cm} (2)

Where $E_1$ and $E_2$ are the local electric field intensity inside the outer layer and inner layer, and $d_1$ and $d_2$ represent the thickness of the outer layer and inner layer, respectively. Meanwhile, according to above two formulas $E_1/e_1 = E_2/e_1$ when $d_1 = d_2$. From this, it can be deduced that $E_1/E_2 = e_2/e_1$ for 5-layer sandwich structure films. Where $E_1$, $E_2$ and $E_3$ are the electric field intensity of the outer layer, middle layer and inner layer, respectively. This is consistent with the simulation results. The average dielectric constant of these 10 samples is equals 20, but the dielectric performances of these materials are diverse because of the difference in polarization distribution. Comparing L3 with L5 and L5a, the dielectric field intensity inside the HB layer is weaker in L3. The proportion of such a layer is 0.5, which is more than that of 0.33 in L5, L5r and 0.2 in L5a. This indicates that it may be able to withstand a stronger electric field before breakdown, which is supported by the experimental observation shown in Figure 6(d). In addition, by comparing L5 with L5r, the relative position of high content and low content layers only determines the distribution of polarization. Therefore, it has little effect on the breakdown strength of the overall composites film. This is also consistent with the experimental results.

Figure 9. The simulation of the electric field intensity distribution in (a) single-layer film, (b) L2, (c) L3, (d) L3r, (e) L3a, (f) L3s, (g) L4, (h) L5, (i) L5r and (j) L5a.
Conclusion

In summary, the structure of multilayer films does affect the overall dielectric properties of these composites. The introduction of HB layers can improve the breakdown strength of films, and the dielectric constant and breakdown strength can be further adjusted by changing the ratio between high breakdown strength layer to high dielectric constant layer. Therefore, multilayer films with two filler contents possess higher content gradients (L2, L3, L3r, L3a and L3s), and exhibit a higher breakdown strength and slightly lower dielectric constant than that of films with lower content gradient, such as sample L5. It is because the proportion of high breakdown layer in multilayer films with two different filler contents is larger. In addition, as a result of the introduction of a high breakdown strength layer, multilayer films demonstrate a higher energy storage density than that of single-layer films. Asymmetrical structure samples (L2, L3a and L4) illustrate slightly lower dielectric constant than that of sandwich structure samples, respectively. From the simulation results, it was shown that the polarization inside the material also exhibits an asymmetrical distribution that reduces the efficiency of charge storage on the electrode plate, but illustrating a higher breakdown strength due to reduced internal electric field. Sample L3s shows a calculated energy storage density of 6.03 J/cm\(^3\), which is 68% higher than L1, and 100% higher than neat P(VDF-HFP). Results show that the preparation of multilayer films is an effective method to adjust the overall dielectric properties by changing the structure while keeping the total content of filler unchanged, so that it can cope with different usage requirements. Moreover, it provides an effective and simple method for directionally adjusting the dielectric constant and breakdown strength of composites by designing multilayer structure. On the other hand, adding different fillers in different layers is also a train of thought for the future work. It is also believed that the construction of multilayer structures can be a feasible method towards to prepare high performance dielectric composites.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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