Structure design boosts concomitant enhancement of permittivity, breakdown strength, discharged energy density and efficiency in all-organic dielectrics

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Abstract: Polymer-based nanocomposites with excellent flexibility and intrinsic high breakdown strength are promising candidates for high energy density capacitors compared to ceramics counterparts. However, their energy density is relatively low due to the trade-off between permittivity and breakdown strength. In this work, the authors proposed a ferroconcrete-like structure for all-organic nanocomposites via combinatorial electrospinning and hot-pressing method. In this structure, polymethyl methacrylate (PMMA) serves as matrix while poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) serves as reinforcement phase. This novel structure is highly effective in breaking the paradox of improved discharged energy density with decreased efficiency, as evidenced by the concurrently improved discharged energy density (~12.15 J/cm³) compared to 8.82 J/cm³ of the matrix) and efficiency (~81.7% compared to 76.8% of the matrix). Compared to conventional blending composite films, samples with ferroconcrete-like structure exhibit higher permittivity, breakdown strength, discharged energy density and efficiency. The superior energy storage performance is attributed to large aspect ratio P(VDF-HFP) fibres distributed perpendicularly to the external field, which brings about the extra enhancement of permittivity. Besides, mechanical properties are improved and restriction on carrier motion is facilitated, leading to enhanced breakdown strength and suppressed conduction. This work provides a new way to design dielectric composite for high energy density and efficiency applications.

1 Introduction
Dielectric capacitors, one of the most important passive element and energy storage device, have been widely used in modern electrical and electronic industry, like stationary power grids, pulsed power system, and hybrid electric vehicles [1–7]. Unlike other energy storage devices based on electrochemical process, dielectric capacitors store and release energy through the rotation of dipoles along with the external electric field, thus deliver the highest power density (on the order of megawatts) and the best rate capability (on the order of microseconds) [8, 9]. With ever-increasing demand for miniaturisation and lightweight of power modules, it is highly essential to improve the energy density of the electrostatic capacitor to reduce the weight and volume of the devices. Basically, the discharged energy density $U_d$ is determined by the electric displacement $D$ and the applied electric field $E$, following the formula $U_d = \int_0^E D dE$ and the formula transforms to a more precise type as $U_d = \frac{1}{2\varepsilon_0 E} E^2$ for linear dielectrics, where $\varepsilon_0$ and $r_d$ represent the vacuum and relative dielectric permittivity, respectively. Since it is the quadratic dependence on $E$, the discharged energy density $U_d$ is largely determined by the breakdown strength $E_b$, which represents the maximum electric field applicable on the capacitor before its failure. Thus, compared to the ceramics counterparts, polymers are the preferred candidates for high energy density capacitors for their intrinsic high $E_b$, not to mention their light weight, flexibility and graceful failure mechanism. For instance, the state-of-the-art commercial polymer dielectric biaxially oriented polypropylene (BOPP) enjoys an energy density of ~5 J/cm³ similar as BaTiO₃ [10], albeit its low permittivity (~2.2) which is near three orders of magnitude lower than that of its ceramic counterparts.

In order to further improve the discharged energy density for polymer dielectrics, it is needed to increase the permittivity since there is not much room for improvement of breakdown strength. One straightforward and effective tactic is to design nanocomposites constituted by polymer matrix with high $\varepsilon_r$ and ceramics fillers with high $E_b$ [11]. Along this line, tremendous efforts have been made by introducing conductive particles [12–16] or high permittivity ceramics [17–25] into the polymer matrix to improve permittivity thus discharged energy density of nanocomposites, and the effects of the shape and concentration of fillers have been thoroughly investigated. Zhang et al. [26] systemically studied that different shapes, distributions and orientations of BaTiO₃ nanofilbers bring about a variety of improvements in permittivity and displacement for polymer-based nanocomposites. However, in order to improve the compatibility between the two phases to get uniform dispersion of inorganic constituents, surface modification with modifiers, like dopamine [27, 28], H₂O₂ [29], phosphonic acid [17, 30] and so forth, is necessary, which makes the fabrication process more complicated and may introduce extra impurities. More importantly, the introduction of inorganic fillers will cause severe electrical field distortion and intensification in the polymer matrix due to the significant mismatch in permittivity between ceramics and polymers [1, 7], which results in a decrease of $E_b$, albeit improvements of $r_d$ for nanocomposites.

Compared to the simple combination of organic and inorganic constituents, the structure design of nanocomposites in mesoscopic scale makes it possible for researchers to tailor various parameters...
for nanocomposites and seems to be a promising route to resolve the paradox between permittivity and breakdown strength. At the beginning, sandwich-structure with three layers of different dielectrics stacked together has been intensively studied [9, 31–34]. In this structure, the outer layers and the inner layer play different roles for either high permittivity or high breakdown strength, resulting in a concomitant enhancement in \( \varepsilon_r \) and \( E_b \) and thus improved discharged energy density \( U_e \). Wang et al. [32] fabricated a series of sandwich-structured barium titanate/poly(vinylidene fluoride) (BT/P(VDF)) nanocomposites with 1 vol.% BT/P(VDF) in the middle and BT/P(VDF) nanocomposites with various content (10–50 vol.%) are adopted as two outer layers. When the outer layer content was 20 vol.%, they achieved a favourable energy density of 18.8 J/cm\(^3\) and the finite element method simulation revealed the interfaces between two different layers could block the development of electrical trees, which accounts for the much higher breakdown strength. With the development of fabrication techniques, researchers expanded the sandwich structure to multilayer structure [35–39] and even gradient structure [26, 40, 41]. Zhu et al. utilised the multilayer coextrusion techniques to investigate a number of polymer films with a multilayer structure, such as PC/P(VDF-HFP) [35, 36], PSF/PVDF [37]. The results revealed that the interfaces between two dielectric layers guided the electrical trees to propagate perpendicularly rather than along to the external field, leading to higher \( E_b \) for multilayer films than that of each component. In our recent work [38], we combined the electrospinning and hot-pressing method to fabricate multilayer nanocomposites with different numbers and orders of the stacking layers and revealed the effects of dielectric/electrode interfaces and dielectric/dielectric interfaces. The results suggested that insulating dielectric were more effective in suppressing the charge injection from electrodes and the polarised ions accumulated in dielectric/dielectric interfaces suppressed the motion of charge carriers across the interfaces and hence hindered the propagation of electrical trees. As a result, an extremely high \( U_e \) of 30.15 J/cm\(^2\) was obtained, together with much enhanced \( E_b \) of 782 MV/m and \( \varepsilon_r \) of P(VDF-HFP)/BTO nanocomposite with 16 layers.

In this contribution, we demonstrate a novel structure, i.e. ferroconcrete-like structure, promising for high energy density capacitor design. In previous research [42], we found that with proper design, this structure could bring about significantly improved mechanical property and enhanced breakdown strength. Herein, linear dielectric polyvinylidene methacrylate (PMMA) is chosen as the matrix, since its intrinsic high breakdown strength and high discharged energy efficiency. In order to improve its permittivity thus discharged energy density, poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) with higher permittivity is employed as reinforcement. Due to the miscibility between PMMA and P(VDF-HFP), polymer blend samples could be fabricated and compared to samples with the ferroconcrete-like structure to reveal the effects of this novel structure. The results show that nanocomposites with ferroconcrete-like structure exhibit higher permittivity compared to that of conventional blending nanocomposites since the much larger aspect ratio of P(VDF-HFP) fibres. Besides, P(VDF-HFP) fibres perpendicular to electric field act as blocking area to suppress the leakage current and improve the out-of-plane Young's modulus, resulting in much-enhanced breakdown strength and improved energy efficiency compared to blending samples. As a result, samples with novel structure show much higher discharged energy density and exhibit concomitant improvement in breakdown strength, permittivity, and discharged energy efficiency, making it a promising route for high energy dielectric capacitors.

2 Experimental

2.1 Fabrication of ferroconcrete-like PMMA/P(VDF-HFP) nanocomposites

P(VDF-HFP) with a weight-average molecular weight of 690,000 was purchased from Arkema and PMMA with a weight-average molecular weight of 210,000 was obtained from Aldalldin. All the solvents were purchased from China National Chemicals Corp. Ltd without further purification. The PMMA granules were dissolved in a mixture of \( N, N \)-dimethylformamide (DMF) and acetonitrile (volume ratio of 3:2) with a concentration of 0.3 g/ml at 50°C in a water bath and then stirred for 10 h to get a homogeneous and stable gel. The P(VDF-HFP) powders were added into another mix solvent of DMF and acetonitrile (volume ratio of 3:2) with a concentration of 0.2 g/ml and stirred for 10 h. The obtained gels were then poured into two individual syringes for the electrospinning process. PMMA and P(VDF-HFP) fibres were electrospun at the same electric field of 1.0 kV/cm and collected onto the same rolling collector to form porous mats containing two kinds of polymer fibres. The rolling rate of the collector was kept relatively low for random distribution of polymer fibres. The feeding rate of two syringes was accurately controlled to get samples with the different volume fraction of P(VDF-HFP). The thicknesses of all final nanocomposite films were kept same by adjusting the electrospinning time. The mats were hot-pressed at 180°C for 0.5 h under 6 MPa pressure (WY-30 T, Weiyi Machinery Equipment Co. Ltd) to form compact nanocomposite films. The as-pressed films were then annealed at 180°C for 7 min followed by quenching in the water of 60°C. Samples with the ferroconcrete-like structure are denoted as ES samples.

2.2 Fabrication of blending PMMA/P(VDF-HFP) nanocomposites

The PMMA granules were dissolved in a mixture of \( N, N \)-DMF and acetonitrile at 50°C in a water bath and then stirred for 10 h to get the homogeneous and stable gel. The P(VDF-HFP) powders of a certain amount were then added into the PMMA gel and stirred for another 10 h. The blending gel was then transferred into a syringe for the electrospinning process. Blending fibres were electrospun at an electric field of 1.0 kV/cm and the thicknesses of all final nanocomposites films were kept the same by adjusting the electrospinning time and feeding rate. The mats were then treated the same as ES samples and the obtained films are denoted as BL samples.

2.3 Characterisations

The morphology of all the samples was characterised by scanning electron microscopy (SEM, ZEISS WWRMLIN compact). X-ray diffraction (XRD, Rigaku D/max 2500 V) and Fourier transform infrared spectroscopy (FTIR, Bruker VERTEX 70 V) were performed to investigate the phase structure. Out-of-plane mechanical properties were measured by Nano Indenter G200 (Keysight). Laser scanning confocal microscopy (LSCM) (ZEISS LSM780) were utilised to analyse the distribution of P(VDF-HFP) fibres in nanocomposites using 543 nm laser. Piezoresonance force microscopy (PFM) measurements were conducted by a commercial scanning probe microscope (Asylum Research MFP-3D). To measure dielectric properties, copper electrodes of 3 mm in diameter and 50 mm in thickness were sputtered on both sides of the films. Dielectric permittivity and loss were tested using a Novocontrol unit in the frequency range of \( 10^{-2}–10^3 \) Hz. The electric displacement-electric field loops \((D-E)\) at 10 Hz were measured using a modified Sawyer–Tower circuit and leakage current versus field were measured by a ferroelectric test system (Radiant Technologies, Inc).

3 Results and discussion

3.1 Morphology and crystal structure of nanocomposites

Combinatorial electrospinning together with the hot-pressing method is employed to fabricate ES samples, as illustrated in Fig. 1. After hot-pressing under proper temperature and pressure, the porous mats are transformed into dense and smooth nanocomposite films free of voids and imperfections, as evidenced by surface and cross-section SEM images of all samples shown in Fig. 1b and Fig. 2. It should be pointed out that since the good compatibility between PMMA and P(VDF-HFP), it seems scarcely possible to tell two polymers apart from the cross-section SEM images of nanocomposite films, not to mention the surface images.
Thus, LSCM with the high spatial resolution is employed to probe the spatial distribution of P(VDF-HFP) fibres in the final nanocomposite films. We introduce a small amount of rhodamine B (1 vol.%) as probes into P(VDF-HFP) gels and follow the same fabrication process of ES samples to get porous mats containing PMMA fibres and P(VDF-HFP) fibre embedded with rhodamine B. As seen from the fluorescent image in Fig. 1c, the green phase refers to rhodamine B, which indicates the existence area of P(VDF-HFP). It could be well distinguished that P(VDF-HFP) is still in its original fibre shape in PMMA matrix. Besides, the P(VDF-HFP) are randomly distributed in the matrix, which could be contributed to the rapid whipping instinct of fibres and slow rotation speed of collector during the electrospinning process [43].

Furthermore, we test samples hot-pressed under different temperatures ranging from 80°C to 200°C, as shown in Fig. 3. For each sample, there are three images to present the microstructure, i.e. fluorescent image, optical image, and a merged image composed of the above two images. It is clear that when the hot-pressing temperature is too low, like 80°C, PMMA and P(VDF-HFP) still remains fibre shape. With the temperature increasing, PMAA transforms into the continuous matrix, while P(VDF-HFP) remains fibre shape, even when the temperature is as high as 180°C. Besides, cross-section PFM images of ES samples support the fibre shape of P(VDF-HFP). For PFM measurement, the ES films were firstly embedded into epoxy and microtomed at −40°C using an ultramicrotome (Leica EM FC6), and the cross-section samples were placed onto glass slides for measurement. As shown in Figs. 1d and e, the amplitude image is in good accordance with the phase image, and the areas showing stronger piezo-response in white colour refer to P(VDF-HFP) due to its intrinsic ferroelectricity. The dots shown in cross-section PFM images imply that the P(VDF-HFP) remains the fibre shape. As seen in Fig. 4, due to the good compatibility between PMMA and P(VDF-HFP) as well as the content of P(VDF-HFP) is relatively low, no extra peaks of P(VDF-HFP) show up in XRD patterns and FTIR spectra.

### 3.2 Dielectric properties of nanocomposites

In order to reveal the effects of ferroelectric-like structure on dielectric properties, the frequency dependence of permittivity for ES samples and BL samples are measured and compared, as summarised in Fig. 5a. Obviously in Fig. 5a, the permittivity of all samples drops with frequency increasing, which arises from the β
relaxation of PMMA. The introduction of P(VDF-HFP) with higher permittivity increases permittivity of nanocomposites at whole frequency range for both ES samples and BL samples and with more P(VDF-HFP) introduced, the enhancements of permittivity are more significant. Comparing the plots of ES samples and BL samples, we can see that ES samples exhibit higher permittivity than that of BL samples at the same content of P(VDF-HFP). For clearly comparison, the variations of permittivity with the volume fraction of P(VDF-HFP) at 10 Hz for ES and BL samples are plotted in Fig. 5b. As seen, for ES samples, the permittivity increases from 4.32 for pure PMMA to 5.03 for nanocomposite with 20 vol.% P(VDF-HFP), while 4.87 for 20 vol.%-BL samples. Also it is obvious that ES samples show higher permittivity than that of BL samples at all contents of P(VDF-HFP). The extra increased permittivity of ES samples over BL samples could be explained by the effective medium theory [44]. Numerous works of literature [26, 27, 45] demonstrate that fillers with large aspect ratio are more effective to improve permittivity of nanocomposites due to their larger dipolar moment and the connected interfaces compared to the spherical counterparts. In this work, the P(VDF-HFP) fibres in the matrix could be regarded as fillers with an extremely large aspect ratio, thus delivering an enhanced permittivity.

3.3 Breakdown behaviour of nanocomposites

Weibull statistics is employed to analyse the measurement results of the breakdown strength of nanocomposites. In principle, the characteristic breakdown strength of dielectric is determined by fitting the data to a two-parameter Weibull distribution equation: \( P(E) = 1 - \exp\left(-\frac{E}{E_B}\right)^\beta \), where \( P(E) \) is the cumulative probability of dielectric failure, and \( E \) is the measurement breakdown data. For two fitting parameters, \( E_B \) represents the scale parameter referring to breakdown strength at the cumulative failure probability of 63.2% and is also considered as the characteristic breakdown strength, while \( \beta \) represents the shape parameter and is associated with the linear regressive fit of the distribution. The fitting results are plotted in Fig. 6a and the Weibull breakdown strength \( E_B \) for both ES and BL samples are summarised in Fig. 6b. As seen, the \( E_B \) of pure PMMA reaches as high as 706 MV/m, which is even comparable to that of commercial BOPP and demonstrates the final films fabricated by this method are rather homogeneous and exhibit very few defects. The most striking feature is the obviously enhanced \( E_B \) in ES samples. As seen, \( E_B \) increases from \( \sim 706 \) MV/m for pure PMMA films to \( \sim 791 \) MV/m for 10 vol.%-ES samples, followed by gradual decrease to a minimum of 756 MV/m with more content of P(VDF-HFP) up to 20 vol.%. To the best of our knowledge, the obtained highest \( E_B \) of 791 MV/m is among the highest Weibull breakdown strength ever achieved in polymer dielectrics. As for BL samples, the \( E_B \) nearly remains the same for all nanocomposite films. When compared to each other, the advantages of structure design are more distinguished. As seen from Fig. 6b, ES samples exhibit much higher \( E_B \) than BL samples at the same P(VDF-HFP) content.

In an effort to understand the improved \( E_B \) in ES samples, the mechanical and electrical properties are characterised. Generally, the electromechanical breakdown is one of the major breakdown mechanisms for polymer dielectrics [46, 47]. The theoretical
Electromechanical breakdown strength $E_{\text{em}}$ could be calculated by the Stark–Garton model [48] as $E_{\text{em}} = 0.606(Y/\varepsilon_0\varepsilon_r)^{1/2}$, where $Y$ represents Young's modulus of dielectrics. Since the external field is applied on the direction perpendicular to the film plane, the out-of-plane mechanical properties determine the dielectric breakdown of polymers. Nanoindentation method is utilised to evaluate the out-of-plane Young's modulus of all nanocomposites. As shown in Fig. 7a, Young's modulus gradually decreases with P(VDF-HFP) content increasing for both ES and BL samples, which results from the fact that P(VDF-HFP) has lower Young's modulus ($\sim$1.32 GPa) than pure PMMA ($\sim$4.8 GPa). Compared to BL samples, ES samples exhibit higher Young's modulus at the same P(VDF-HFP) content. The improvement of mechanical properties induced by structure design has been demonstrated in a number of nanocomposites [26, 49, 50] in which ‘hard’ fillers with better mechanical properties are used. In this work, we demonstrate that even when the introduced filler is ‘soft’, structure design can also bring about better mechanical properties for nanocomposites than the conventional method, thus may contribute to higher breakdown strength. Therefore, it suggests the ferroconcrete-like structure is a universal and effective approach to tailor the mechanical properties and alleviate deleterious electromechanical breakdown strength.

In addition to electromechanical breakdown, the electrical breakdown behaviour should also be taken into account, especially under high electric field and room temperature in our condition. For comparison, the leakage current density of 10 vol.%-ES and 10 vol.%-BL samples under different electric fields are measured and presented in Fig. 7b. The leakage current mainly arises from the mobility of charge carriers inside the nanocomposites or injected from the electrodes. For both 10 vol.%-ES and 10 vol.%-BL, the leakage current increases with the external field increasing. The leakage current of 10 vol.%-ES is lower than that of 10 vol.%-BL at all electric fields. It suggests that ferroconcrete-like structure...
P(VDF-HFP) and PMMA can serve as deep traps due to their excellent compatibility to restrict the motion of carriers under rapidly changing electric field. As a result, the measured $D_i$ strongly related to conduction is suppressed in 5 vol.%-ES and 10 vol.%-ES samples. The enhanced $D_m$ and suppressed $D_i$ could bring about better energy storage performance. The discharged energy density $U_e$ and stored energy density $U$ are derived by calculating the area enclosed by the charged/discharged curve and ordinate, and the efficiency $\eta$ is obtained by $\eta = U_e/U$. The discharged energy density $U_e$, and efficiency $\eta$ as a function of the electric field for ES samples are presented in Figs. 10a and b. As seen, after P(VDF-HFP) introduced, significant improvements of $U_e$ are obtained owing to the concomitant enhancement of $E_B$ and $E_F$. The highest $U_e$ is achieved as 12.15 J/cm$^3$ for 10 vol.%-ES samples due to its extremely high $E_B$, which is near 40% higher than pure PMMA, albeit the content of P(VDF-HFP) is so low. Besides, the high $U_e$ is not achieved at the cost of comprised efficiency. As seen from Fig. 10b, the ES samples show comparable efficiency $\eta$ to pure PMMA at the same electric field, and at high field 5 vol.%-ES and 10 vol.%-ES samples even enjoy higher energy efficiency than PMMA due to the improved $D_m$ and suppressed $D_i$. To better distinguish the advantages of this ferroconcrete-like structure, $U_e$ and $\eta$ of the ES samples and BL samples are compared in Figs. 10c and d, respectively. While the $U_e$ of BL samples increases monotonically from 8.82 to 9.70 J/cm$^3$ for 20 vol.%-BL with more P(VDF-HFP) introduced, the $U_e$ of ES samples first increases rapidly from 8.82 to 9.70 J/cm$^3$ for pure PMMA to 12.15 J/cm$^3$ for 10 vol.%-ES, followed by slightly decreasing to 10.90 J/cm$^3$ for 20 vol.%-ES. Since the breakdown strength of BL samples is comparable to each other, the $U_e$ is mainly determined by permittivity, as for ES samples, the breakdown strength dominates the trend of $U_e$. It is obvious that ES samples enjoy much higher $U_e$ than BL samples at the same P(VDF-HFP) content and the biggest extra enhancement is near 31.5% for 10 vol.%-ES over 10 vol.%-BL, as a result of simultaneous improvements of permittivity and breakdown strength. The efficiency $\eta$ of all samples are compared at 700 MV/m, which is extremely high and near the breakdown strength of PMMA. As seen, while BL shows superior performance on suppressing leakage current. The interface regions between polymers could be at play in restricting the motion of charge carriers and hence suppressing the leakage current. For ES samples, the interface regions are mainly perpendicular to the external field direction due to the layer-by-layer electrospinning process, which makes it more effective in restricting the motion of charger carriers compared to BL samples. Besides, similar to multilayer structure nanocomposites, the interfaces perpendicular to the electric field can hinder the breakdown process by guiding the electric trees to propagate along the interfaces thus perpendicularly to film plane, which results in higher breakdown strength in ES samples. This also explains why 10 vol.%-ES enjoys higher breakdown strength than pure PMMA, albeit its lower Young's modulus and relatively higher leakage current.

### 3.4 Energy storage performance of nanocomposites

The $D$–$E$ loops of all samples are obtained using a modified Sawyer–Tower circuit, as shown in Fig. 8. To better present the effects of introducing P(VDF-HFP), the maximum displacement $D_m$ and remnant displacement $D_r$ of ES samples are derived from the loops as a function of electric field and summarised in Fig. 9. As seen from Fig. 9a, similar to the trends of permittivity, $D_m$ increases monotonously at the same electric field with P(VDF-HFP) content increasing. However, due to its highest breakdown strength, $D_m$ of 10 vol.%-ES (~3.73 μC/cm$^2$) is even higher than that of 15 vol.%-ES (~3.63 μC/cm$^2$). The $D_r$ of all samples show similar behaviour to pure PMMA, i.e. when $E$ is relatively low (~500 MV/m), $D_r$ increase slightly with $E$ increasing, while $D_r$ increases more significantly when the electric field is high enough. This mainly arises from the fact that under the high electric field, the charge injection at electrodes becomes more severe and leakage current increases exponentially [51]. A striking feature is that under the high field, the $D_r$ of 5 vol.%-ES and 10 vol.%-ES are even smaller than that of pure PMMA. When the content of P(VDF-HFP) keeps relatively low, the harmful effect on overall insulativity is little. On the contrary, the interface regions between P(VDF-HFP) and PMMA can serve as deep traps due to their
samples exhibit slightly lower $\eta$ than pure PMMA. ES samples have higher efficiency when the content of P(VDF-HFP) in smaller than 15 vol.%. For 5 vol.%-ES and 10 vol.%-ES, the $\eta$ is even higher than 80% at such an extremely high field, which is among the highest efficiency for polymer nanocomposites containing P(VDF-HFP). Similar to leakage current, interfaces perpendicular to the external field direction could be more effective in restricting the motion of carriers, thus leading to suppressed conduction loss and improved energy efficiency for ES samples compared to BL samples.

Since the parameters related to energy storage performance of dielectrics include permittivity, breakdown strength, discharged energy density and efficiency, it is better to look into the overall parameters when judging the performance of nanocomposites. Along this line, radar charts based on the data of ES samples and BL samples are presented in Figs. 11a and b, respectively. Taking into account the fact that it is more meaningful to evaluate the enhancement over the matrix rather than the absolute value, the ratios of $\varepsilon_\text{e}/\varepsilon_\text{m}$, $E_\text{e}/E_\text{m}$, $U_\text{e}/U_\text{m}$, $\eta_\text{e}/\eta_\text{m}$ at 700 MV/m are used here for comparison, and $\varepsilon_\text{m}$, $E_\text{m}$, $U_\text{m}$, and $\eta_\text{m}$ represent the permittivity, breakdown strength, discharged energy density and efficiency of the matrix, respectively. The dotted squares in black refer to the data of pure PMMA. As seen from Fig. 11a, the dotted square is obviously wrapped by quadrangles of ES samples, which means the concurrent improvements in permittivity, breakdown strength, discharged energy density and efficiency are achieved in nanocomposites with ferroconcrete-like structure. The $\varepsilon_\text{e}/\varepsilon_\text{m}$, $E_\text{e}/E_\text{m}$, $U_\text{e}/U_\text{m}$ are obviously larger than 1, especially for $U_\text{e}/U_\text{m}$. As in Fig. 11b, we can see the quadrangles of BL samples mainly overlap the dotted square, which means the improvements induced by the conventional structure are slight.

4 Conclusions

In summary, PMMA/P(VDF-HFP) nanocomposites with ferroconcrete-like structure, in which PMMA serves as matrix while low content of P(VDF-HFP) as reinforcement phase, are fabricated with combinatorial electrospinning and hot-pressing method. The introduction of P(VDF-HFP) with high permittivity improves the permittivity of nanocomposites, and the continuous P(VDF-HFP) fibres with large aspect ratio in this ferroconcrete-like structure give extra enhancement of permittivity compared to the conventional structure at the same P(VDF-HFP) content. The interface regions perpendicular to the external electric field can improve the mechanical properties of nanocomposites and block the motion of carriers, leading to enhanced breakdown strength and suppressed conduction. As a result, the discharged energy density and efficiency of ES samples are significantly improved compared to pure PMMA and BL samples. An extremely high breakdown strength of $\sim 791$ MV/m together with a high energy density of 12.15 J/cm$^3$ are obtained in 10 vol.%-ES, which is about 40 and 32% higher than $U_\text{e}$ of pure PMMA and 10 vol.%-BL, respectively. Besides, higher discharged energy density is obtained without sacrificing the efficiency, and higher charge-discharge efficiency (>80%) is achieved at an extremely high electric field of 700 MV/m. Nanocomposites with ferroconcrete-like structure exhibit concomitant enhancement of permittivity, breakdown strength, discharged energy density and efficiency, and this novel structure is much more effective than conventional structure and provides new thoughts for high energy density capacitors design.

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Fig. 11 Radar charts of comprehensive performance for (a) ES samples, (b) BL samples

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