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Waterborne Nanocomposites with Enhanced Breakdown Strength for High Energy Storage

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ABSTRACT: Polymers have been considered as promising materials for dielectric energy storage because of their high breakdown strength, favorable flexibility and processability. The achievable energy density of polymers is however limited by their intrinsic low dielectric constant. Until today, most of them are either melt-extruded at high temperatures or solution-processed in harmful organic solvents. Making high-energy polymeric dielectrics via environmentally friendly manners has been a long standing challenge. Herein, a water-based technique is employed to prepare all-polymeric dielectrics consisting of poly(vinylidene fluoride) (PVDF) latex nanoparticles dispersed within a polyvinyl alcohol (PVA) matrix. These waterborne nanocomposites, processed at low temperature, demonstrate great promise in resolving the paradox between dielectric constant and breakdown strength. A high energy density of 8.1 J/cm^3 is thus achieved at $\sim 515 \text{ MV/m}$, which is 300% greater than that of each polymer component. Moreover, with an appropriate load resistance, the nanocomposite can release the stored energy at a rate of microseconds, giving rise to a power density of 1.13 MW/cm^3 that is nearly 400% higher than that of benchmark biaxial oriented polypropylene dielectric films.

KEYWORDS: waterborne nanocomposite, polymer latex, energy density, power density, breakdown strength

INTRODUCTION

Energy storage technologies have been pursued to improve the grid scale load leveling for instantaneous and periodic fluctuations, particularly with ever-increasing production of renewable energy that heavily relies on meteorological conditions.¹⁻³ Current technologies, such as lithium-ion batteries and supercapacitors, have high gravimetric energy density but are unable to provide extremely rapid response to the peaks in energy production or demand. Stabilizing the load on the grid scale requires energy storage devices with very fast energy uptake and delivery. Dielectric capacitors store energy electrostatically in the form of electric displacement induced by the applied electric field. This energy storage mechanism offers intrinsically high power density, high operating voltage, and long work lifetime⁴⁻⁷. However, such mechanism also causes limited energy densities that are approximately three orders of magnitude less than fuel cells or Li-ion batteries.^{8,9} Such limitation requires greater amount of materials to be used, and makes this approach more costly. Therefore, developing dielectric materials with improved energy density is imperative to enable the continuous miniaturization and increased functionality of the cutting-edge electrical power systems. Generally, the energy density U_e of dielectrics is determined by the applied electric field E and the associated electric displacement D .² It can be mathematically expressed by

$$U_e = \int_{D_{max}}^0 E dD \quad (1)$$

Therefore, the key to improve the energy density of dielectric materials is to achieve a high breakdown strength E_b (the maximum electric field that the material can withstand without undergoing electrical breakdown) and a large electric displacement D_{max} .

Compared with inorganic dielectrics, polymers are attractive due to their high breakdown strengths, low losses, flexibility and ease of processing.¹⁰⁻¹³ Until today, many polymers, such as biaxial oriented polypropylene (BOPP), polyethylene terephthalate (PET), polycarbonate (PC) and polyvinyl alcohol (PVA), have been deployed to make film capacitors.^{2,10,14} However, the low dipole moments of the chemical bonds in these polymers result in low dielectric constant ($k < 4$), leading to a low energy density ($< 5 \text{ J/cm}^3$) even under the electric field near breakdown strengths. Conversely, polar polymers, such as poly(vinylidene fluoride) (PVDF)-based ferroelectric polymers, are particularly promising for energy storage due to the high polarization of the C-F bonds and the spontaneous orientation of dipoles in the crystalline domains.^{15,16} However, the strongly coupled dipoles and large ferroelectric domains in these polymers cause high energy barriers for ferroelectric switching, leading to pronounced hysteresis loops and in turn to low charge/discharge efficiency (the ratio of U_e to the total stored

energy density). Chemical methods (i.e., copolymerization) or high-energy radiation have been developed to increase the efficiency by limiting ferroelectric losses of PVDF based polymers through changing the ferroelectric polymers into relaxor-ferroelectric ones.^{17, 18}

In spite of the intrinsic improvements of energy density by modifying macromolecular structures, most of efforts have been devoted, in the past decades, to the composite approach, a more versatile extrinsic strategy.^{2, 10, 11, 19, 20} This approach capitalizes upon the combination of different components/phases with high dielectric strength and high dielectric constant respectively via engineering their interfaces or interphases.²¹⁻²⁶ Indeed, a large number of ceramic nanoparticles with different dimensionalities, such as highly polarizable BaTiO₃ nanoparticles or nanofibers²⁷, or high- E_b boron nitride nanosheets^{8, 28}, have been added to PVDF-based polymers to achieve concomitant enhancement of dielectric constant and breakdown strength. Nevertheless, the high density of ceramics and the inorganic/organic discrepancy in physicochemical properties usually lead to sedimentation and unexpected inhomogeneous distribution of nanofillers.²⁹ This actually poses a great challenge on the mass production of high-quality dielectric nanocomposite films.

Being parallel with the inorganic/organic approach, blending lightweight polymers with different polar groups on the side chains has been also explored.³⁰⁻³⁸ The similar solubility and chemical structure of polymers allows for easier processability and good adaptability to the roll-to-roll stretching fabrication. For instance, high- E_b and low-loss linear dielectric polymers, such as PET³⁸ and PC³⁶, have been multilayered with PVDF-based polymers to serve as a barrier for the treeing propagation through the film thickness. This method largely suppresses the conduction losses, improves the breakdown strength, and eventually enhances the energy density. In addition to the layered 2-2 composite configuration, rubber nanoparticles³³ and thermoplastic polyurethane (TPU)³⁵ that bear high breakdown strength have been also introduced into PVDF matrix to formulate 0-3 nanocomposites with elevated energy density.

Here we propose another 0-3 nanocomposites that are waterborne and made by mixing PVDF latex and water soluble PVA. Being different from the continuous phase of PVDF in previously reported composites, the low-cost PVDF latex nanoparticles are adopted as discrete polarizable domains in high- E_b PVA matrix. The moderate permittivity and conductivity contrast between PVDF and PVA is expected to achieve less distorted local electric field. We found that the presence of small amount (3 wt%) of PVDF nanoparticles within PVA matrix can concurrently increase the permittivity and breakdown strength from 6.9 to 8.0 and from 438 MV/m to 515 MV/m respectively, giving rise to an energy density of 8.1 J/cm³. Moreover, the nanocomposite can release the stored energy on a load resistor of 10 k Ω at a rate of

microseconds, leading to a power density of 1.13 MW/cm^3 . Both of the energy and power density are nearly 400% greater than those of benchmark BOPP. The use of water-based techniques can provide the environmentally friendly aspect to both processes and consumption of current high-energy dielectric films.

EXPERIMENTAL SECTION

Materials. PVA was obtained from Sigma-Aldrich under the trade name of Mowiol 18-88 (CAS number: 9002-89-5) with a molecular weight $M_w=195\,000 \text{ g/mol}$ and a degree of hydrolysis of 99%. PVDF latex was supplied by Arkema (Kynar Aquatec ARC Latex) with an initial concentration of solid content of 44 wt%.

Fabrication of PVDF/PVA nanocomposites. PVA was first dissolved in deionized water at 95°C in an oven overnight, and then magnetically stirred at 300 rpm for 2h at room temperature. The solution was afterwards filtrated under vacuum to obtain a fully dissolved aqueous solution. The PVA concentration was measured at 10.3 wt%. As schematically illustrated in **Figure 1a**, various amount of PVDF latex was mixed with the PVA solution by magnetic stirring at room temperature for 4 h. The final solute concentration of different aqueous mixtures is kept at 1.1 wt% by adding different amount of deionized water. The final solid PVA nanocomposites possessed different PVDF contents. The nanocomposite films were prepared by a solution-casting method. In detail, 5ml well-mixed solution was casted onto a petri dish of poly(methyl methacrylate). Water was then evaporated at 55°C for 90 min under an infrared light. The dry film was peeled off and put into vacuum oven at 110°C for 20h. The PVDF/PVA nanocomposite films are transparent (**Figure 1b**) and their thickness ranges from $15 \mu\text{m}$ to $25 \mu\text{m}$.

Characterizations of PVDF/PVA nanocomposites. The dielectric properties of the films were recorded as a function of frequency (from 10^{-1} Hz to 10^6 Hz) at room temperature by an impedance analyzer (MaterialsMates 7260, Italia). The dielectric breakdown strength and electric polarization-electric field (P - E) loops were measured at room temperature in silicone oil via a PolyK ferroelectric polarization loop and dielectric breakdown test system. Fast discharge experiments were carried out through a capacitor charge/discharge system (PolyK Technologies). Before the characterizations, each sample was coated with aluminum electrodes to ensure a good contact. Transmission electron microscopy (TEM) images of PVDF/PVA nanocomposites were taken via a Hitachi H600 microscope operating at 75 kV. To make samples for TEM characterizations, the pure PVDF latex or the mixed solutions with different mass ratios between PVDF latex and PVA solution were directly dropped on a carbon-coated

copper films (200 mesh), which was followed by a room-temperature evaporation of water to formulate an ultrathin layer. Wide-angle x-ray diffraction (XRD) was tested on a Rigaku Nanoviewer (MicroMax 007HF) with a rotating anode coupled to a confocal Max-Flux® Osmic mirror operating at a wavelength of 1.5418 Å. The recorded spectra were corrected by subtraction of the reference noise. Differential scanning calorimetry (DSC) measurements were performed using TA Instrument Q2000 under dry nitrogen atmosphere. About 3 mg specimens were heated from 30 to 250 °C at a rate of 10 °C /min with three cycles, and the second curve was selected to analyze.

Figure 1. (a) Water-based processes to incorporate PVDF nanoparticles into PVA matrix and make dielectric nanocomposite films. (b) Photograph of a transparent PVA composite film filled with 3 wt% PVDF latex nanoparticles.

RESULTS AND DISCUSSION

Morphologies of PVDF latex and their nanocomposites. TEM was performed on pristine PVDF latex and their nanocomposites to investigate the dispersion state and the morphology of PVDF latex nanoparticles in PVA matrix. As shown in **Figure 2a**, PVDF latex particles are spherical with a diameter of 149 nm. **Figure 2b-f** reveals the morphology evolution of nanocomposites with increasing the PVDF content from 1wt% to 5wt%. At concentrations below 3 wt%, the natural good dispersibility of PVDF particles can ensure the formation of isolated PVDF nanodomains in PVA matrix (**Figure 2b-d**). By contrast, as the concentration is

beyond 4wt%, the particles start to coalesce and form clustering due to the attractive interactions (**Figure 2e-f**) during current water-based processing.

Figure 2. (a) TEM image of PVDF latex particle, showing a diameter of 149 nm. TEM morphologies of PVDF/PVA nanocomposite films with various loadings of PVDF nanoparticles: (b) 1 wt%, (c) 2 wt%, (d) 3 wt%, (e) 4 wt%, and (f) 5 wt%.

Dielectric performances of PVDF/PVA nanocomposite films. The dependences of dielectric constant on the frequency are shown in **Figure 3a**. Dielectric constants of all the polymer composites tend to decrease with increasing frequency. At each frequency, the dielectric constant increases monotonously with the PVDF content. Nevertheless, all the dielectric constants of composites fall into the interval of the two single polymer components. The conductivity and loss tangent are weakly affected by the presence of PVDF at frequencies beyond 100 Hz (**Figure 3b-c**). By contrast, differences of conductivity and losses are observed as the frequency decreases down to 100 Hz and below. The lowest conductivity and loss tangent are obtained at 3wt% of PVDF nanoparticle. The variation of dielectric constant and losses with the concentration of PVDF nanoparticles is presented in **Figure 3d**. At 100 Hz, the dielectric constant increases from 6.9 to 8.1. In spite of the enhancement in dielectric constant, the losses at 100 Hz keep stable with varying PVDF content and remain at a level below 0.05.

Figure 3. (a) The dielectric constant, (b) AC conductivity, and (c) loss tangent of PVDF/PVA films as a function of frequency at room temperature. (d) The dielectric constant and loss tangent at 100 Hz vary with PVDF nanoparticle loading.

Generally speaking, when a current flows across the two-material interfaces in a heterogeneous system, charges will accumulate at the interface between two materials with different relaxation time ($\tau = \varepsilon/\sigma$, where ε is the dielectric constant and σ is the conductivity).³⁹ In the present case, the relaxation time of PVDF and PVA is on the same order of magnitude. The induced interfacial polarization is actually very weak, and has a limited contribution to the improvement of dielectric constant of PVA composites. By contrast, large interface areas can be generated upon addition of even small amount of nanofillers, and induce substantial effects in polymers. We characterized the crystalline structure changes of PVA by XRD and DSC. As shown in Figure S1, PVDF nanoparticle exhibits strong nucleation ability, substantially increases the crystallinity of PVA while not impacting the size of crystallites. Intriguingly, the dielectric constant curve presented in **Figure 3d** resembles the crystallinity curve (Figure S1b), revealing the correlation between the crystalline structures and the dielectric constant in PVA

films. The results suggest that the largely formed crystallites have strong dielectric response to the applied electric field owing to the spontaneous orientation of dipoles in the crystalline domains, and thus contribute predominately to the increase of dielectric constant. This mechanism is supported by the experiment results of Zhang *et al.*⁴⁰ on poly(arylene ether urea)/alumina nanocomposites, in which 0.21 vol% of 20-nm-sized alumina nanoparticles can lead to more than 50% increase in the dielectric constant.

Dielectric breakdown strength of PVDF/PVA nanocomposite films. For a linear dielectric, the dielectric constant is independent of the applied electric field. Consequently the energy density U_e is linearly proportional to the production of permittivity and the square of electric field. Several reports show that the addition of high- k nanoparticles can largely enhance the dielectric constant yet at the expense of the breakdown strength.^{2, 14, 41} Due to the quadratic dependence on E_b , the energy density of the composites is however found to be inferior to neat polymers in spite of the improved permittivity. It is highly desirable to achieve an E_b that is superior to the neat polymers. The characteristic electric breakdown strength is generally analyzed with a two-parameter Weibull distribution function:⁴²

$$P(E) = 1 - e^{-\left(\frac{E}{E_b}\right)^\beta} \quad (2)$$

where $P(E)$ is the cumulative probability of dielectric failure, E is the measured breakdown strength for each specimen, E_b is the characteristic breakdown strength that corresponds to a ~63.2% probability of failure, and β is the so-called shape parameter that evaluates the scatter of data. Herein, the E_b and β are calculated from a linear fitting using Weibull failure statistics (**Figure 4**), and the values are listed in **Table 1**. The high β values indicate the structural uniformity and integrity of the investigated composite films. The E_b of pure PVDF and PVA films are 222.6 MV/m and 437.9 MV/m, respectively. It is noted that the breakdown strength of PVDF latex film is lower than that (350-400 MV/m) of typical PVDF films that are solution-casted or melt-extruded.^{33-35, 43} The discrepancy arises from the film processing. In the present case, the wet thin film containing suspended colloidal PVDF nanoparticles is dried on a substrate, the evaporation of water concentrates the nanoparticles into a closed packed array. The capillary pressures created by liquid menisci between colloidal particles lead to cracking of the dried film.⁵ Without any additive, it is difficult, if not impossible, to obtain a uniform large-area PVDF film without microcracks. It is such morphological defects that weaken the capability of the obtained dry films to sustain a high electric field. By contrast, the introduction of a small amount PVDF nanoparticles into PVA does not deteriorate but greatly promotes the

breakdown strength of the PVA matrix. The breakdown strengths of all the polymer composites are superior to that of PVA. At an optimum PVDF content (3 wt%), the maximum breakdown strength reaches 514.7 MV/m, showing an improvement of 18%. Similar enhancements have been also observed in polymer composites filled with high- k yet low- E_b ceramic nanofillers at low filler loadings.^{40, 44-47} The addition of even small amount of nanofiller can chemically or physically form large-area interfaces in a nanocomposite.^{2, 10, 22, 45, 48, 49} The dielectric properties of the interfacial regions can slightly differ from the bulk polymer matrix.^{2, 50} They have been proven capable of suppressing space charges as deep trapping sites at high electric fields, and limit thereby the probability for breakdown.^{44, 45, 47} Actually, the breakdown strength enhances with increasing the interfacial area as a result of adding more nanoparticles. Nevertheless, beyond a certain filler content (in our case, 3wt %), the interfacial regions would percolate, and thus carriers can transport instead of being restrained in the interfacial regions. The density and mobility of carrier increases in the composites, leading to a decrement in breakdown strength^{44, 45, 47} (**Figure 4, Table 1**). Here, the effect of newly generated interfaces is also validated in a composite even composed of two polymeric phases with moderate permittivity and conductivity contrast. In addition, previous theoretic simulations⁵¹ and experiment work^{40, 52} show that elevated crystallinity in semicrystalline polymers can substantially limit the high-field conduction losses by reducing the mean free path for the mobile charge. As compared to virgin PVA, the improved crystallinity (Figure S1B) of PVA composites should be also responsible for the augmentation of the breakdown strength. Last, it should be noted that the enhancements in the dielectric constant and breakdown field in composites with inorganic nanoparticles occur in an extremely narrow nanofiller composition range.^{40, 44, 47} By contrast, all the composites with PVDF loading ranging from 0.5 wt% to 5wt% can exhibit improved breakdown strength as compared to the virgin PVA. This feature allows for a much broader operation window for the preparation of high- E_b PVA composites.

Table 1. The E_b and β of pure PVA, PVDF, and their composites at various mass ratios.

PVDF content (wt%)	E_b (MV/m)	β
0	437.9	25.2
0.5	444.5	19.1
1.0	461.5	15.3
2.0	479.4	12.5
3.0	514.7	19.5
4.0	499.9	18.8
5.0	477.8	15.6
100	222.6	12.4

Figure 4. Failure probability of dielectric breakdown deduced from Weibull distribution for neat PVA, PVDF and their composites with various PVDF particle loadings.

High-field polarizations of PVDF/PVA nanocomposite films. We first compare the P - E loops of different films up to a given electric field which approaches the breakdown strength of pure PVDF film. As shown in **Figure 5a**, being similar with the trend observed for the dielectric constant (**Figure 3a**), all the $P_{\max}$ of the composites fall into the interval of the two single polymer components. Nevertheless, the hysteresis loops of all the composites are much slimmer than those of pure PVDF and PVA, indicating that the introduction of PVDF nanoparticles could effectively constrain the movement of free charge carriers, resulting in reduced conduction losses at high fields. It is particularly interesting to investigate the polarizations of composite with 3 wt% PVDF at much higher electrical field as it shows the highest breakdown strength. With increasing the electric field, the $P_{\max}$ increases yet the composites show higher losses at higher fields (**Figure 5b**), which is as a result of the bulk conduction in PVA matrix. Based on the P - E loops of pure PVDF, PVA, and their composites at different fields until their breakdown strength, the discharged energy density is calculated and shown in **Figure 5c**. Apparently, below ~ 250 MV/m, pure PVDF film shows the maximum energy density $U_e = 3.4$ J/cm³, while the energy densities of PVDF/PVA composites are inferior to this value but still higher than that of pure PVA film. Intriguingly, the energy density of the composite with 3 wt% of PVDF reaches 8.1 J/cm³ at 510 MV/m, which is three folds higher than that ($U_e = 2.4$ J/cm³) of neat PVA, demonstrating a synergistic effect by coupling PVDF and PVA.

Figure 5. (a) *P-E* loops of pure PVA, PVDF and PVDF/PVA nanocomposite films with various PVDF contents. (b) *P-E* loops of PVA nanocomposite film with 3 wt% PVDF at different electric fields. (c) The discharged energy density and (d) charge/discharge efficiency as a function of electric field for pure PVA, PVDF, and PVDF/PVA nanocomposite films.

For practical applications, it is also important to evaluate the charge/discharge efficiency, η , which is defined as

$$\eta = \frac{U_e}{U_s} = 1 - \frac{U_l}{U_s} \quad (3)$$

where U_s , U_e , and U_l are the stored, discharged energy and energy loss, respectively. U_l is calculated by the numerical integration of the closed area of the hysteresis *P-E* loops. As shown in **Figure 5d**, the efficiency of all the films decreases with the applied electric field, because of the more pronounced conduction losses at higher fields. It is clearly shown that the efficiency is enhanced with the introduction of PVDF nanoparticles as compared to neat PVA film. This is another evidence for the charge carrier constraint as a result of the incorporation of small amount of PVDF nanoparticles. Consequently, at the maximum electric field, the efficiency of 3 wt% nanocomposite is about 0.6, higher than that (~0.3) of neat PVA. The energy storage

performances of pure PVA and its composites have been summarized and shown in **Figure 6**. The overall desirable high-field properties demonstrate great potential of PVDF/PVA composites for the dielectric energy storage applications. The maximum breakdown strength of PVDF/PVA composites can compare with most of previously reported polymeric dielectric materials, as listed in **Table 2**. The improvement of energy density (defined as U_e/U_m , where U_m is the discharged energy density of base materials) is much higher than those of the reported polymeric dielectrics. The charge/discharge efficiency (60%) is relatively lower than the counterparts. However, it should be noted that most of the polymeric dielectrics are either melt-extruded at high temperatures or solution-processed in harmful organic solvents. Our strategy relies on environmental benign processes, has great promise for the “green” manufacturing of next-generation polymeric dielectrics.

Figure 6. The breakdown strength, discharged energy density, and charge/discharge efficiency as a function of PVDF content for the PVDF/PVA composite films. The discharged energy density and the charge/discharge efficiency were measured at the maximum electrical field that they can sustain before electrical breakdown.

Table 2. Comparison of the energy storage performances of different polymeric dielectric materials.

Materials	Processing methods	E_b MV/m	U_e J/cm ³	U_e/U_m	η
MBS/PVDF ^{33 a}	solution casting in DMF ^j	535	9.8	2.2	62%
TPU/PVDF ^{35 b}	solution casting in DMF	538	10.4	2.3	n/a
PET/PVDF ³⁴	melt-mixing and hot-pressing	453	7	1.6	n/a
P(VDF-TrFE-CFE)/PVDF ^{53c}	solution casting in DMF	665	19.6	1.6	n/a
PET/PMMA/P(VDF-HFP) multilayer film ^{38 d}	melt coextruding	1000	17.4	1.5	n/a
PC/PVDF layered film ³⁷	melt coextruding	650	11	1.8	60%
P(VDF-HFP)/PMMA ^{31 e}	solution casting in DMAC ^k	475	11.2	2.6	86%
P(VDF-CTFE)-g-PS copolymer ^{54 f}	grafting copolymerization and solution casting in THF ^l	520	12	1.2	70%
P(VDF-TrFE-CTFE)-g-PMMA copolymer ^{55 g}	grafting copolymerization and solution casting in DMF	500	10.5	2.6	70%
Bis(double-stranded) Block Copolymer ⁵⁶	tandem metathesis polymerization and solution casting in organic solvents	370	9.9	n/a	84%
PMGS-ArTU ^{57 h}	polymerization and solution casting in DMF	419	3.2	n/a	87%
c-BCB/BNNS ^{8 i}	drop casting from DMM ^m solution and thermally crosslinking	447	2.5	n/a	95%
BaTiO ₃ @TiO ₂ /P(VDF-HFP) ⁵⁸	solution casting in DMF	500	9.95	1.3	65%
PVDF latex/PVA	water-based process	514	8.1	3.4	60%

^aMethyl methacrylate-butadiene-styrene/PVDF. ^bThermoplastic polyurethane/PVDF. ^cPolyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene/PVDF. ^dPoly(ethylene terephthalate)/poly(methyl methacrylate)/poly(vinylidene fluoride-co-hexafluoropropylene). ^ePoly(vinylidene fluoridehexafluoropropylene)/poly(methylmethacrylate). ^fPoly(vinylidene fluoride-co-chlorotrifluoroethylene)-*graft*-polystyrene. ^gpoly(vinylidene fluoride-co-trifluoroethylene-co-chlorotrifluoroethylene)-*graft*-poly(methyl methacrylate). ^hCross-linked polysiloxane-aromatic thiourea. ⁱcrosslinked divinyltetramethyldisiloxane-bis(benzocyclobutene)/boron nitride nanosheets. ^jN,N-Dimethylformamide. ^kDimethylacetamide. ^lTetrahydrofuran. ^mDipropylene glycol dimethyl ether.

In addition to the high energy density, power energy storage requires a fast discharge rate.^{15, 16, 59} We used a high-speed capacitor discharge circuit (**Figure 7a**) with a high-voltage MOSFET (metal oxide semiconductor field effect transistor) switch to measure the discharge speed of the nanocomposite with 3%wt PVDF and commercial BOPP film. Both samples were first charged at 200 MV/m, followed by discharging across a 10 k Ω load resistor in series with the polymer capacitor. The discharging curves are shown in **Figure 7b**. The voltage, $U(t)$, across the load resistor, R_L , decreases exponentially with time. The fitting to the curves by the equation $U(t) = U_0 e^{-(t/\tau)}$ yields the time constant, τ . For the waterborne nanocomposite (Figure S2a-c), obtained τ varies from 0.40 μ s to 0.63 μ s as broadening the fitting time range. Likewise, τ of BOPP film capacitor varies from 0.38 μ s to 0.65 μ s (Figure S2d-f). Both sample capacitors have nearly identical time constant for a given fitting time range, which actually allows for fairly comparing their power densities. Furthermore, the deduced $R_L C$ values are 0.59 μ s and 0.45 μ s for waterborne nanocomposite and BOPP films respectively. Both of them fall in the range of τ yielded by fitting. The change of τ obtained from the fitting to different time ranges can be associated to the increased effect of equivalent series resistor (ESR) of samples at later discharge process.¹⁶ Based on the discharging curves, the instant power P_e can be calculated by¹⁶

$$P_e = \frac{U(t)^2}{R_L} \quad (4)$$

The discharged energy density U_e of the dielectric material is further calculated by¹⁶

$$U_e = \frac{\int_0^\infty P_e dt}{V} = \frac{\int_0^\infty \frac{U(t)^2}{R_L} dt}{V} \quad (5)$$

where V is the volume of dielectric materials. The calculated energy density is plotted in **Figure 7c** as a function of time. The discharge time is defined here as the time that is needed to reach 95% of the final discharge energy in a load resistor.⁶⁰ In this regard, the nanocomposite releases a stored energy of 1.329 J/cm³ at a rate of 1.172 μ s, while the rate for BOPP is 1.168 μ s for releasing a stored energy of 0.299 J/cm³. Accordingly, the waterborne nanocomposite shows a superior power density of 1.13 MW/cm³ to that of BOPP (0.26 MW/cm³). The cyclic charge/discharge was performed on both samples under an applied field of 200 MV/m to evaluate the stability of the materials. As shown in **Figure 7d**, there is not degradation over 1000 cycles of charge/discharge of the waterborne nanocomposite with 3wt% PVDF.

Figure 7. (a) Circuit diagram of the charge/discharge experiment operated with a high-voltage MOSFET switch. The losses of samples are treated as an ESR. The voltage (b) and discharged energy density (c) as a function of time. The BOPP and waterborne nanocomposite films (3 wt% of PVDF) have respectively a thickness of $9.8 \mu\text{m}$ and $24 \mu\text{m}$, which correspond to capacitance of 45 pF and 59 pF respectively. (d) Cyclic charge/discharge performances of both samples under electric field of $200 \text{ MV}/\text{m}$.

CONCLUSION

In summary, waterborne polymer nanocomposites are prepared by mixing low-cost PVDF latex and water soluble polymer PVA, followed by a solution-casting method. Compared with pure PVA film, the dielectric response of waterborne nanocomposites is improved because of the formation of more crystallites in PVA matrix as a result of the introduction of a small amount of PVDF latex nanoparticles. Moreover, due to the charge carrier constraint effect associate to the newly generated large-area interfaces, the nanocomposite with an optimum PVDF contents (3%) shows a breakdown strength as high as $515 \text{ MV}/\text{m}$ and an energy density of $8.1 \text{ J}/\text{cm}^3$, which respectively show improvements by 18% and 238% as compared to pure PVA film. The waterborne nanocomposites with a microsecond discharge rate exhibit a power

density on the level of 1.1 MW/cm³. It is anticipated that this work opens an environmentally begin route to boost the energy storage performances of polymer nanocomposites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/>.

DSC curves and XRD patterns of pure PVA and its composites with various PVDF loadings; The degree of crystallinity and estimated size of crystallites of PVA as a function of PVDF loading; Fitting of the discharging voltage as a function of time for capacitors based on waterborne nanocomposite as well as commercial BOPP film.

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Notes

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Waterborne Nanocomposites with Enhanced Breakdown Strength for High Energy Storage

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Supplementary Figures

Figure S1. (a) DSC curves and (c) XRD patterns of pure PVA and its composites with various PVDF loadings. (b) The degree of crystallinity as a function of PVDF loading. The crystallinity of samples is determined by evaluating the enthalpy of fusion and comparing it to the enthalpy of fusion of 100% crystalline PVA. The calorimetric crystallinity is defined as $X_c(\%) = [\Delta H_c / ((1 - \Phi) \cdot \Delta H_m)] \times 100$. X_c is the weight fraction of crystallinity, Φ is weight fraction of PVDF, ΔH_c is the enthalpy of fusion at the melting point for each sample, ΔH_m is the enthalpy of fusion of the totally crystalline polymer measured at the equilibrium melting point and equal to 138.6 J/g for PVA. (d) Estimated size of crystallites of PVA as a function of PVDF loading. The average size of crystallites is estimated from Scherrer equation, $D = K\lambda / B \cos \theta$, where D is the mean size of the crystalline domains. K is the shape factor, which has a typical value of about 0.9. λ is the X-ray wavelength (0.15418 nm in our case). B is line broadening at half the maximum intensity (FWHM, in radians). θ is the Bragg angle in radians.

Figure S2. Fitting of the discharging voltage as a function of time for (a-c) waterborne nanocomposite as well as (d-f) commercial BOPP film. The τ yielded from the fitting is indicated in the figure. Red curves are the fitting and black curves are the experimental data. The BOPP and waterborne nanocomposite films (3 wt% of PVDF) have respectively a thickness of 9.8 μm and 24 μm , which correspond to capacitance of 45 pF and 59 pF respectively.