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Recent advances in rational design of polymer nanocomposite dielectrics for energy storage

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ABSTRACT

Polymer nanocomposites dielectrics have attracted increasing attention for electric energy storage applications in recent years due to their enhanced dielectric performance by combining the high permittivity of nanoparticles and the high electrical breakdown strength of polymer matrix. Herein we present a review of the recent advances in the modelling of dielectric energy storage and model-based rational design of polymer nanocomposite dielectrics. The synthesis strategies and dielectric property behaviors of polymer nanocomposite dielectrics are also discussed. In particular, this review focuses on key strategies and analytical models for substantial improvements in energy density of composite dielectrics including interfacial design, microstructural engineering and new high-dielectric filler materials. By applying machine learning techniques in conjunction with the analytical models, new designs have emerged. To demonstrate the practical applications of polymer nanocomposite dielectrics, a summary is presented of some recent examples of scale-up production of energy storage devices in electrical vehicles, pulsed weapons systems and power electronics. Finally, challenges and new application opportunities of polymer nanocomposite dielectrics are discussed.

1. Introduction

Nowadays, the efficient energy storage systems, including batteries, supercapacitors and solar cells, have individually demonstrated their efficacy in practical applications. Present scenarios related to polymers or polymer composites are presented in terms of recent progress in supercapacitors, batteries and solar cells for energy storage. Recent advance of high mesoporous carbon prepared through the pyrolysis of enables the supercapacitor polymers [1], electrode for high-energy-density supercapacitors, where a high specific capacitance is harvested at high discharge rate. Ladder-like donor-acceptor polymers with twisted structure acting are constructed as electrode material for flexible supercapacitors [2]. Aligned carbon nanomaterials as robust and high performance electrodes enable the design of stretchable supercapacitors, showing their enhanced robustness and electrochemical performance under pronounced deformations for wearable electronics [3]. In addition, both metal-organic frameworks [4] and two-dimensional covalent organic frameworks [5] show great promising in active materials for supercapacitors owing to their high surface areas, changeable pore sizes, alterable shapes and diverse architectures. However, the disadvantage of supercapacitors falls in their limited energy density.

Lithium-ion battery, as one of most efficient and prevalent electrochemical energy storage devices, much effort is devoted into increasing either the capacity of electrolytes or improving the energy density, durability and safety of electrolytes. UV induced crosslinking is conducted to hinder the crystallite formation and improve ionic conductivity in polymer solid electrolyte membranes [6] or composites [7], showing their excellent cycling stability and Coulombic efficiency in all-solid-state li-ion batteries. In addition, room temperature ionic liquid based electrolytes prepared by UV induced free radical polymerization technique [8] or multipolymer electrolyte membrane by oxygen

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Fig. 1. Schematics illustrate the electric displacement as a function of electric field [31]. Reproduced with permission from Elsevier.

inhibited UV-crosslinking [9] offer a new insight for designing high energy cathode. The hybrid solid electrolytes after experiencing solvent-free preparation process provide a scalable approach for Li-based battery [10]. To realize the design of smart rechargeable commercial Li-based batteries [11] and multivalent metal and metal-ion rechargeable batteries [12], recent progress in terms of various organic [12] or metal-organic polymer electrodes [13] is proposed to achieve the high density, better safety and excellent stability. However, the inevitable environmental pollution and lacking resources in Li-based battery are always the critical issues. On the other hand, photocatalysis as another feasible energy storage technology, is commonly used to degrade the organic pollutants as well as produce the hydrogen, where photo-assisted isoelectric point method [14] is employed to achieve great effectiveness in degradation of pollutants and hydrogen production. Nanostructured conjugated polymers are prepared for sustainable and versatile energy devices beyond solar cells [15] by altering their structures and incorporating various functional moieties [16].

To address the demands of ever increasing energy requirements of the global community, it is critical to integrate renewable energy sources, which are often intermittent, with high energy-efficiency storage [17,18]. Over the last two decades significant advances have been accomplished in renewable energy sources such as wind and solar [19, 20]. The rapid expansion in renewable energy capturing capability has prompted an intense interest in high efficiency and environmentally friendly energy storage technologies, such as fuel cells, batteries and dielectric based capacitors [18,21,22]. Among these, high-voltage dielectric capacitors hold considerable promises owing to their superior power density and rapid rate of charge-discharge and desirable cycling stability [23,24]. In this context, the energy density, structural safety and processability remain major issues for dielectric capacitors [19,25].

Compared with conventional ceramic dielectric materials, polymer/ inorganic nanoparticles nanocomposite dielectrics have sparked keen interests for electric energy storage applications [17], owing to ability to combine the high permittivity of ceramics dielectrics fillers with polymer matrix materials of high electrical breakdown strength [19,26]. One major issue with such composite dielectrics is that the enhancement in dielectric permittivity ε_r usually comes at the expense of reduced breakdown strength E_b [27]. The degradation of breakdown strength is generally caused by the following factors: (a) severe local electric field distortion at the interface of the polymer matrix and inorganic ceramics fillers caused by the large difference in dielectric permittivity [28,29]; (b) agglomeration of the fillers and defects in the composites resulting from the incompatibility between polymers and fillers [30]. Therefore, it remains a great challenge to simultaneously improve the dielectric permittivity and breakdown strength in polymer composite dielectrics [27,31].

To improve the breakdown strength E_b , several approaches have been proposed for polymer composites: (a) surface functionalization to improve the compatibility and dispersion of inorganic fillers in polymers [32]; (b) core-shell structure of inorganic fillers with the shell layer having smaller dielectric permittivity to mitigate the distortion of the local electric field [33]; (c) alignment of fillers in a direction perpendicular to the external applied electric field during operation to provide ordered scattering centers/tortuous paths for free electrons during breakdown [28,34,35]; (d) use of inorganic fillers with high thermal conductivity to improve heat conduction and prevent the adverse temperature rise [28,36]. To achieve the simultaneous improvement of ε_r and E_b , the inorganic ceramic fillers with high dielectric permittivity and fillers with superior thermal conductivity were investigated [37]. Furthermore, the topological arrangement of placing inorganic nanoparticles at the outer region and inorganic nanofibers in the center region has been studied [38,39]. By incorporating conductive fillers below their percolation thresholds [40,41] using a two-step freeze drying technique [37], composites were demonstrated that featured improved dielectric property and breakdown strength, and hence greatly improving energy density. In this case, it is vitally important to prevent the increase in dielectric loss while increasing the dielectric permittivity [35,42].

In this review, the recent advances of polymer nanocomposite dielectrics are summarized, including the comprehensive synthetic strategies, major techniques to improve the energy density/efficiency/ stability and new applications of polymer nanocomposite dielectrics. Section 2 describes the critical parameters affecting the energy storage capability and characterization methods. Section 3 summarizes and compares the currently developed approaches in structural engineering,



Fig. 2. Electrical displacement (D) as a function of electric field (E) [44]. Reproduced with permission from Oxford University Press.

which includes either surface functionalization or structural design. Section 4 reviews the mechanism related to enhance the ε_r or/and E_b in polymer composite dielectrics. Section 5 discusses the polymer composite dielectrics toward large scale-up production. The final section outlines remaining challenges and future applications of polymer nanocomposite dielectrics for energy storage.

2. Crucial factors for polymer composites dielectrics

2.1. Different types of dielectrics

The electric displacement of dielectric materials as a function of electric field is demonstrated in Fig. 1, showing various types of dielectrics. In general, energy storage capacitors are classified into five kinds: linear dielectrics, paraelectric, anti-ferroelectric dielectrics and ferroelectric dielectrics (relaxor ferroelectrics included). Energy loss increases when the nonlinearity of the dielectric behavior becomes more pronounced. Among all capacitors available at present, the relaxor ferroelectric dielectrics have superior potentials as a promising alternative for energy storage applications due to their large saturated remnant electrical displacement D_{max}, small remnant electrical displacement Dr and moderate breakdown strength Eb. More importantly, their efficiency can reach up to 90%, indicating that less energy will dissipate in the form of heat during discharging. For instance, the introduction of A site and B site complex ions in the relaxor ferroelectrics of ABO3 can destroy the long-range ferroelectric order and form polar nano-regions (PNRs), which can substantially broaden and flatten the dielectric-temperature curves [43].

The energy storage density U_e during the polarization process can be calculated based on the integral of the green shaded area in Fig. 2(a). Alternatively, when remnant electrical displacement D_r is known, energy density U_e of dielectrics is determined by the electrical displacement (D) and electric field (E) via $U_e = \int_{D_r}^{D_{max}} EdD$ (Fig. 2(b)). The amount of energy density dissipated during the discharge process is



Fig. 4. Dielectric permittivity of Ni/BaTiO₃+PVDF composites as a function of Ni content [48]. Reproduced with permission from American Institute of Physics.

defined as U_{loss} , which can be calculated based on the integral of blue shaded area in Fig. 2(a). Therefore, the energy-storage efficiency η can be expressed as $\eta = \frac{U_t}{U_{e^+}+U_{loss}} \times 100\%$. However, linear dielectrics, such as polymers and their based composites, show almost no energy loss and their energy density is determined by breakdown strength based on the formula $U_e = \frac{1}{2}DE_b = \frac{1}{2}\varepsilon_r\varepsilon_0E_b^2$, where ε_r denotes the relative dielectric permittivity, ε_0 the dielectric permittivity of a vacuum and E_b the breakdown strength. Based on this formula, it is clear that the energy density of a dielectric material is limited by its dielectric permittivity and breakdown strength. To achieve a high energy density, it is essential to develop dielectric materials with both high dielectric permittivity and high breakdown strength.

2.2. Dielectric permittivity

To achieve the improved dielectric permittivity, dielectric nanofillers of insulating, semiconducting and conducting compounds have been generally employed through dispersion into a polymer matrix [45]. Moreover, small volume fraction of nanofillers added into the elastic polymer matrix can maintain the flexibility of the polymer. Fig. 3 shows electrostatic energy storage capacitors including vacuum capacitors and capacitors with both conventional dielectrics and dielectrics of high dielectric permittivity. In Fig. 3(b), the improved charge q_m can be attributed to the energy needed for polarizing the inside dielectrics. When common linear dielectrics are replaced with high dielectric permittivity dielectrics, a further increase in charge q_p is observed due to the introduced dielectrics, as illustrated in Fig. 3(c), which consists of



Fig. 3. Schematic diagrams illustrating the stored energy in electrostatic capacitors under the applied electric field. (a) Vacuum capacitor, (b) capacitor with dielectrics inside to reach a charge of $Q = q + q_m$, (c) capacitor embedded with dielectrics of high dielectric permittivity to achieve an accumulated charge of $Q = q + q_m + q_p$ [46]. Reproduced with permission from Royal Society of Chemistry.



Fig. 5. Breakdown strength evolution process of polymer nanocomposites with (a)–(b) nanoparticles filler and (c)–(d) nanofibers at the same volume fraction. (e) Breakdown strength evolution process for polymer nanocomposites with either nanoparticles or nanofibers as a function of filler volume fraction. Insets indicate the electric field distribution [49]. Reproduced with permission from John Wiley and Sons.

three parts of energy originating from the polarization of nanofiller, the interface between nanofiller and polymer matrix, and the interaction between nanofillers, respectively.

To quantify the dielectric permittivity of polymer nanocomposites in terms of the properties of the filler and the matrix, various models have been developed. According to the percolation theory, when conductive nanofillers approaching the percolation threshold are dispersed into a polymer matrix, the dielectric permittivity of this composite would expect a rapidly rising dielectric permittivity when the percolation threshold is approached [41]. For instance, Tu et al. [47] prepared PVDF based percolative composites by using two dimensional MXene nanosheets as conductive filler, achieving a very high dielectric permittivity of 10^5 . In addition, Dang et al. [48] achieved a gradually increasing dielectric permittivity when tuning the added Ni content below 0.2 vol %. Moreover, a rapid enhancement of dielectric permittivity was observed when Ni content approached the volume fraction of 0.20 vol% (Fig. 4).

2.3. Breakdown strength

As noted in Section 2.1, the energy density is proportional to the dielectric permittivity, but is quadratic function of the breakdown strength, implying that the breakdown strength is the most important parameter for achieving high energy density. However, the critical influence of dielectric permittivity cannot be ignored, because an increase in the breakdown strength is often accompanied by a reduction in the dielectric permittivity. This can be attributed to the local electric field concentration caused by the large difference of dielectric permittivity at the interface of polymer matrix and fillers, which gives rise to an inverse relationship between the dielectric permittivity and the breakdown strength. One of the promising ways to maintain the high breakdown strength while increasing dielectric permittivity is to lower the difference in the dielectric permittivity of the polymer matrix and the fillers. This can be realized by employing structural engineering techniques, such as surface functionalization, interfacial design and topological design. These structural engineering techniques will be clarified in the following sections.

In addition to the experimental investigation, numerical simulations using the finite element analysis method are also effective ways to guide the design of dielectric composites of high breakdown strength [50]. An incomplete breakdown theory was developed to explain the partial breakdown path formed in high electric field region, which can arise when high contents of dielectric fillers are incorporated into polymers. The aggregation of fillers is a key issue that limits the use of high concentration of dielectric fillers. Structure designs play a very significant role in altering the current density in polymer composites. By tuning the designed structures in polymer composites (Fig. 5), spatial distribution of leakage current density with changeable intensity is clearly reflected via the phase field simulation [51], which gives a roadmap for designing polymer dielectrics with high breakdown strength.

Moreover, considering the difference in dielectric strength between nanocomposite containing nanoparticles and nanofibres, the dynamic evolution of the breakdown strength can be predicted. Fig. 5 shows the breakdown strength evolution process of polymer composites with either nanoparticles or nanofibers. It can be observed that nanofiber nanocomposites can sustain a larger electric field than that nanoparticle nanocomposites [49].

2.4. Effect of interface

The incorporation of nanomaterials, either insulating or conductive, significantly affects the overall properties of dielectric nanocomposites. In nanocomposites, the role of the interface between fillers and the matrix is an important because (a) large surface areas of nanomaterials create a large interaction zone between the nanomaterials and polymer matrix; (b) changes in the surface morphology of the polymer matrix surrounding the fillers; (c) the internal field change caused by the small size of the nanomaterials; (d) space charge distribution; (e) scattering effect. The introduction of a second phase such as nanofiller into the polymer matrix can affect the dielectric permittivity and breakdown strength of polymer dielectric by the space charge distribution or through scattering effect [30]. In addition, the size of nanomaterials will also influence the formed microstructure that affects the electrical displacement. The interfacial charge density can be predicted by the Maxwell-Wager-Sillars theory, which was used to describe charge formation and decaying between varied materials [52]. Rogti et al. employed the modified Maxwell-Wagner-Sillars theory to investigate the interfacial space charge behavior of multilayer polymer composites [53].

In the work by Prateek et al. [17], polymer nanocomposites with un-functionalized and functionalized nanofillers with a variety of phases, which range from conventional two-phase to three-phase nanocomposites, were explored in terms of various parameters, such as dielectric property, breakdown strength, energy density and flexibility (Fig. 6(a)). Owing to the nanofiller incorporation, numerous interfaces have been created because of the small nanofiller dimension. The



Fig. 6. (a) Polymer nanocomposites with different phases; (b) diffuse electric double layer produced by a positively charged particle in a polymer matrix containing mobile ions, along with the resulting electrical potential distribution $\psi(r)$; conduction via diffuse double layers in a composite system; (c) multicore model for the interface of polymer and nanoparticles [17]. Reproduced with permission from American Chemical Society.

surface of a nanofiller tends to be wholly or partly charged due to the chemical potential difference between nanofiller and polymer matrix. With the polymer matrix responding to the counter charge in the adjacent nanofiller surface, an electrical double layer consisting of stern layer and diffuse layer forms, resulting from the charge distribution of nanofillers based on Lewis's model [54]. The electrical potential distribution $\psi(r)$ was also demonstrated in Fig. 6(b) as a function of the distance from nanofillers.

In addition to Lewis's model, Tanaka's model [55] was also developed to describe the interfaces in polymer nanocomposites, which show triple layers consisting of bonded layer, bound layer and loose layer (Fig. 6(c)). Compared with other two layers, the bonded layer is strongly bonded with either organic or inorganic layers in either hydrogen bonding, van der Waals force and covalent or ionic bonds. Polymer chains will actively respond to the bound layer, forming the second layer which is determined by the interaction between nanofiller and polymer matrix. In terms of the loose layer, various chain configurations form in polymer matrix. Therefore, selecting appropriate bound layer or loose layer will alter the dielectric property, consequently affecting the energy density of polymer composites.

2.5. Other parameters in affecting polymer composite dielectrics

In polymer composite-based dielectrics, the size, shape and morphology of filler particles have great effect on the performance of composite dielectrics. For instance, the influence of particle size and morphology on dielectric tunability of nanocomposites is investigated, showing an enhanced dielectric property with increased size of platelike $(Ba_{0.6}Sr_{0.4})TiO_3$ nanoparticles in PVDF textured composites [56]. By using the two-step molten salt method, plate-like particle size can be altered via controlling the soaking time. Moreover, through the simulation of dielectric property in composites, a shape factor in dielectric theoretical model enables the characterization of particle size, which is well consistent with the experimental result. Consequently, the optimal dielectric of composites is achieved at a certain size of nanoparticle in $(Ba_{0.6}Sr_{0.4})TiO_3/PVDF$ nanocomposites.

Core-shell like structured fillers [56,57], surface functionalized two-dimensional fillers [58] and hollow structured fillers [59] are introduced to reduce the aggregation and reduce the probability of forming conductive path in composites, where multiple interfaces in hierarchical structures or gradient layered structures [60] are formed to suppress the dielectric loss of composites [61]. To further investigate the effect of ceramic filler geometry on breakdown strength and dielectric property, polymer nanocomposites with BST nanowires were compared to that of other fillers of BST nanoparticles, BST nanorods, BST nanocubes and pure polymer [62], showing the enhanced electrical displacement and reduced inhomogeneity of electric field distribution in polymer composites from experimental and simulation results. The enhanced energy density is eventually achieved in composites with BST nanowires with BST nanowires.



Fig. 7. Comparison between experimental results and predicted values from various theoretical models: (a) Experimental results and theoretical predictions from various models in BTO/P(VDF-HFP) composite dielectrics [73]; reproduced with permission from Springer Nature. (b) Comparison between Lichtenecker model, modified kerner model and SC-MET model [72]; reproduced with permission from American Chemical Society.

compared to other nanofillers.

3. Models for dielectric permittivity and breakdown strength

A number of mechanisms have been put forward to clarify the electric field distribution and breakdown process in terms of dielectric permittivity and breakdown strength, which include the influence of electronic, thermal, mechanical, heat, etc.

3.1. Models for dielectric permittivity

To investigate the frequency-dependent dielectric permittivity on polymer composite dielectrics, theoretical models were developed to analyse and predict the various sequences with different volume fractions of dielectric filler. Below a specific volume fraction of dielectric filler, the theoretical models such as Lichtenecker model, Maxwell-Wagner model and Yamada model showed good correlation with experimental results. However, at higher volume fraction of dielectric filler, a three-phase model was necessary to obtain a reasonable correlation by taking into consideration the fraction of aid void [63].

3.1.1. Wiener rule

The dielectric permittivity of a two-phase composite can be simply calculated based on a rule of mixture or the Wiener rule [17,63]:

$$\varepsilon_{com} = \nu_m \varepsilon_m + \nu_f \varepsilon_f \tag{1}$$

where ε_{com} , ε_m and ε_f stand for the dielectric permittivity of composites, polymer matrix and dielectric filler, respectively, while ν_m and ν_f are the volume fractions of polymer matrix and dielectric filler, respectively, with $\nu_f = 1 - \nu_m$. For a two-phase composite material system, this rule presents a clear expression of effective dielectric permittivity after assuming the homogeneity and continuity in composites.

3.1.2. Lichtenker's model

Besides the Wiene rule, another modified model named Lichtenker's model was also employed to calculate the dielectric permittivity based on the assumption of random spatial distribution of filler shapes and orientations in composite dielectrics [64]:

$$\log \varepsilon_{com} = \nu_m \log \varepsilon_m + \nu_f \log \varepsilon_f \tag{2}$$

Therefore, dielectric permittivity of composites can be calculated based on this Lichtenker's model, which is independent of approaches adopted in composites fabrication.

3.1.3. Maxwell-Garnett equation/Maxwell-Wagner model

$$\varepsilon_{com} = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_f + 2\nu_f(\varepsilon_f - \varepsilon_m)}{2\varepsilon_m + \varepsilon_f - \nu_f(\varepsilon_f - \varepsilon_m)}$$
(3)

Yu et al. reported [65] that the improved dielectric permittivity and dielectric loss was obtained in BTO/PVDF nanocomposites, whose results were well consistent with the predicted valued based on Maxwell-Wager model. The Maxwell-Wager model is based on the assumption of continuous and isotropic spherical particles in composites system.

3.1.4. Bruggeman self-consistent effective medium approximation

By modifying the Maxwell–Garnett equation/Maxwell-Wagner model, Bruggeman self-consistent effective medium approximation was viable to predict the dielectric permittivity of composites with high volume fraction of dielectric filler [66]:

$$\frac{\varepsilon_f - \varepsilon_m}{\varepsilon_{com}^{1/3}} = \frac{(1 - \nu_f)(\varepsilon_f - \varepsilon_m)}{\varepsilon_m^{1/3}}$$
(4)

Song et al. [67] reported that a large increase in dielectric permittivity was experimentally obtained at a small content of $BaTiO_3$ nanowires, which was well consistent with the value predicted by the effective medium theory. To account for the significantly improved dielectric constant of $Ag@TiO_2$ /polytetrafluoroethylene composites, an effective medium percolation model was used to predict the dielectric permittivity of this three-phase composites, showing a good correlation with experiments results [68]. The Bruggeman self-consistent effective medium approximation is believed to be an extension of Lichtenker's model, where more complex situations in composites with anisotropic inclusions will be considered.

3.1.5. Yamada model

Dielectric permittivity was studied based on Yamada model [69] for a continuous and homogeneous binary system of polymer and dielectric composites with high loadings of dielectric filler: H. Hu et al.

$$\varepsilon_{com} = \varepsilon_m \left[1 + \frac{\eta \nu_f (\varepsilon_f - \varepsilon_m)}{\eta \varepsilon_m + (\varepsilon_f - \varepsilon_m) (1 - v_f)} \right]$$
(5)

As reported in Yu et al. [70], the Yamada model was used to predict the values compared with those of achieved from experimental results. Shape factor η in equation (5) enables the discussion and analysis of particles with various size and morphology. The simulated values of the dielectric permittivity showed a good agreement with experimental results in composites at a low concentration of BaTiO₃. However, the model failed to predict the dielectric permittivity at a concentration of 60 vol% BaTiO₃, which was considered due to the agglomeration and air voids occurred in the composites.

3.1.6. Modified kerner model

$$\varepsilon_{com} = \frac{\varepsilon_m \nu_m + \varepsilon_f \upsilon_f \left[\frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \right] \left[1 + \frac{3\nu_f (\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \right]}{\nu_m + \nu_f \left[\frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \right] \left[1 + \frac{3\nu_f (\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \right]}$$
(6)

The interaction between adjacent fillers was considered to achieve the dielectric permittivity for a two-phase composite based on modified Kerner model [71].

In Fig. 7, comparison between experimental results and predicted values from various theoretical models is performed to reveal the effectiveness of models used in predicting the theoretical results of dielectric permittivity. In Fig. 7(a), Results predicted by Lichtenker's model and Maxwell-Wager model are quite consistent with experimental results when the volume fraction of filler reaches up to 50%, while both modified Kerner model and Yamada model present a higher dielectric permittivity for composites. Results predicted by Wiener rule are also demonstrated as comparison. It is noted that all the models show an increased dielectric permittivity as the volume fraction of filler increases, which is contradictory with experimental design showing an optimum dielectric permittivity at a certain volume fraction of filler. In Fig. 7(b), the modified Kerner model was applied to predict the dielectric permittivity values, which were then compared with experimental results [72]. Below a certain amount of filler loading, this model correlated well with experimental results, while a distinct discrepancy was revealed at a high filler content. To achieve the perfect fitting of permittivity across the entire range of filler content, other models such as Lichtenecker model and SC-MET were also attempted although no model has been found to be valid at high loadings.

3.1.7. Percolation theory

Percolative polymer nanocomposites have attracted enormous attention in energy storage due to the achieved large dielectric permittivity at the adjacent of percolation threshold [74]. A transition of insulating to conducting state happens at the percolation threshold in the polymer composites due to the formed continuous networks. The



Fig. 8. Dielectric constant of carbon@BTO/P(VDF-HFP) as a function of the filler volume fraction of carbon@BTO. Theoretical dielectric constant was predicted based on the equation of (6) [76]. Reproduced with permission from Royal Society of Chemistry.

breakdown strength experiences a sudden drop, although this phenomenon is not expected to occur. The relationship between dielectric permittivity and volume fraction of conducting filler is given as follows [40,41,66,75]:

$$\varepsilon_{com} \propto \varepsilon_m \left(\nu_c - \nu_f\right)^{-q} \tag{7}$$

where ν_c is the volume fraction at the percolation threshold and q is a material property.

By incorporating conductive filler below the percolation threshold, the dielectric permittivity of polymer nanocomposites was greatly enhanced as the conductive filler increased to the vicinity of percolation threshold through insulator-conductor transition [77]. In Fig. 8, the experimental results showed a good agreement with the percolation theory, where a dramatically enhanced dielectric permittivity was obtained at the vicinity of the percolation threshold [76]. The mechanism behind the percolation theory is the existence of minicapacitor effect, where minicapacitor networks form in polymer matrix [29]. Owing to the adjacent conductive nanofillers and a thin layer of dielectric existing in between, thousands of minicapacitors have been formed. When nanofiller loading approaching the critical percolation threshold, the dielectric permittivity increases rapidly [78], leading to a very high capacitance. The large capacitance contributes to a significant increase in the intensity of local electric field, where the migration and accumulation of charges will be promoted at the interface of nanofiller and polymer matrix [74].



Fig. 9. Schematic diagrams of polarization charges exist in (a) P(VDF-TrFE-CFE); (b) MXene/P(VDF-TrFE-CFE) metal-insulator-metal (MIM) capacitors under the external applied electric field. (c) Schematic illustration of dipoles formed between the MXene surface atoms (F, O) and atom H of the polymer backbone [47]. Reproduced with permission from American Chemical Society.



Fig. 10. Breakdown strength, dielectric permittivity and energy density calculated based on the phase-field model [49]. Reproduced with permission from John Wiley and Sons.

In Fig. 9, PVDF based composites were prepared using two dimensional MXene nanosheets as fillers. A substantial high dielectric permittivity of about 80000 at 10 kHz was obtained, with the dielectric loss of 0.05. The mechanism related to percolation theory can also be used to explain the substantial improvement of dielectric permittivity [47]. However, low breakdown strength, high energy dissipation and poor voltage endurance are becoming the remaining issue to be resolved to achieve the full potential of conductive fillers in practical applications.

Much effort has been devoted to improving the high breakdown strength while maintaining the relatively high dielectric permittivity [79]. Functionalizing conductive nanofillers with an insulating layer is a promising approach to achieve the high dielectric permittivity with reduced dielectric loss in polymer nanocomposites, showing the suppressed energy dissipation. For instance, Han et al. reported that adding the SiO₂-coated reduced graphene oxide nanosheets to a poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) polymer matrix creates a composite with a greatly reduced dielectric loss and the stable dielectric loss in the frequency range of 300 kHz to 3 MHz as well as a remarkable high breakdown strength of 80 kV/mm at the percolation threshold [80].

3.2. Models for breakdown strength

3.2.1. Dielectric breakdown model (DBM)

The dielectric breakdown model [81] describes the breakdown patterns formed in a polymer composite dielectrics, where the dielectric fillers are assumed to be homogeneously distributed in the polymer matrix. At the point of dielectric breakdown, the electrical trees formed in the composites propagate along the dielectric medium without causing any inhomogeneity. The tree channel growth is affected by the electrical field. The probability of a tree channel growth is proportional to the electrical field *E* to power of η . Therefore, the relationship between the probability and electric field can be expressed as follows [81, 82]:

$$p(i, k \to k', k') = \frac{(E_{i,k'})^{\eta}}{\sum (E_{i,k'})^{\eta}}$$
(8)

where *P* is probability, (\vec{t}, \vec{k}) stands for the tree channel growth sites, *E* is the electrical field and η is the exponent.

Based on equation (9), both experimental and calculated electrical tree behaviors can be determined on fractal dimension and failure probability. The fractal dimension can be derived from a function called scaling behavior, which covers all the sites belonging to the electrical tree. The relationship between scaling behavior and fractal dimensional can be written as follows.

$$C_r = C_0 r^{D-2} \tag{9}$$

where C is the scaling behavior, r is the radius of a circle to include all the sites and D is the fractal dimension.

The probability of failure is usually affected by the propagation time, which controls the number of channels accumulating into the electrical tree. In addition, the failure probability also satisfies a two-parameter Weibull distribution model [83], which can be shown as follows:



Fig. 11. The effect of nanofiller alignment on the breakdown strength of polymer nanocomposites [49]. Reproduced with permission from John Wiley and Sons.



Fig. 12. Surface functionalization of various types of filler by using different kinds of methods [32]. Reproduced with permission from Royal Society of Chemistry.

$$P(t) = 1 - \exp[-(t/\alpha)^{\beta}]$$
(10)

where α is parameter to characterize the time t and β is a shape parameter.

In Wang et al.'s work, a two-parameter Weibull statistic model (equation (10)) was used to analyse the breakdown strength behaviour of the nanocomposites based on the experimental results, which reflects

the characteristic breakdown strength at a probability of 63.2% [84].

3.2.2. Modified DBM model

To meet the practical sequence with dielectrics randomly distributed into the polymer matrix, the DBM model was modified to account for the contribution by dielectric patterns in terms of the fractal dimension and the Weibull distribution parameters [63].

$$P(i, k \to i', k') = \frac{\left(\frac{E_i', k'}{L_i}\right)^{\eta}}{\sum \left(\frac{E_i', k'}{L_i}\right)^{\eta}}$$
(11)

where *P* is probability, (\vec{l}, \vec{k}) stands for the tree channel growth sites, *E* is the electrical field and η is the exponent. L_i was introduced as the pertaining breakdown channel length. L_i can be expressed as follows:

$$L_i = L_0 - \frac{L_0}{a_i} \tag{12}$$

where L_i stands for the varied breakdown channel length and a_i is the distance between conducting particles. The value of a_i varies depending on whether conducting particles accounted for in the electrical tree.

3.2.3. Phase-field model

To improve the effective dielectric permittivity of polymer nanocomposites, ceramics dielectric fillers were introduced into the polymers. In this case electric field tends to concentrate at the interface between dielectric fillers and the matrix, which degrades the breakdown strength. In addition, as the applied electric field exceeds a critical value, cracks may initiate and propagate along weak paths, resulting in a complete breakdown. To describe the damage initiation and evolution in polymer dielectrics, a phase-field model has been developed [85].

In order to achieve both local field distribution and crack propagation details, a continuum phase-field model [49] was modified to

Table 1

Summar	y of dielectric fillers an	d surfactants used in	dielectric comp	osites and their diel	lectric, breakdown streng	th, energy den	sity properties.
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Polymer matrix	Dielectric filler content	Surface modifier	Dielectric permittivity (1 kHz)	Dielectric loss (1 kHz)	Breakdown strength (kV/mm)	Energy density (J/ cm ³)	References
P(VDF-HFP)	50% vol BaTiO ₃ particles	Phosphonic acid	31	0.03	215	3.2	[72]
PVDF	50 wt% BaTiO ₃ particles	Carboxylic acid	32	0.04	325	9.89	[87]
Poly(vinyl alcohol) (PVA)	40% vol BaTiO ₃ particles	Gallic acid	51	0.08	144	0.554	[88]
PVDF	40 vol% BaTiO ₃ particles	Polyvinylprrolidone (PVP)	65	0.02	10	0.03	[89]
PVDF	20 vol% BaTiO ₃ particles	NXT-105	41	0.03	200	3.54	[65]
PVDF	10 vol% BaTiO ₃ particles	Tetrafluorophthalic acid	35	0.04	285	5.1	[90]
P(VDF-HFP)	20 vol% BaTiO ₃ particles	Hydantoin resin	20	0.04	330	8.13	[91]
PVDF	4 vol% BaTiO ₃ particles	Titanate coupling agent	12	0.04	517	11.27	[92]
PVDF	10 vol% BaTiO ₃ particles	Polyvinyprrolidone (PVP)	14	0.02	336	6.8	[70]
PVDF	2.5 vol% SrTiO ₃ nanofibers	Polyvinylprrolidone (PVP)	11	0.04	380	6.8	[93]
P(VDF-HFP)	5% vol BaTiO3 nanowires	Fluoro-polydopamine	14	0.04	480	12.87	[94]
PVDF	7.5 vol% Ba _{0.2} Sr _{0.8} TiO ₃ nanowires	Ethylenediamine	17.5		484.3	14.86	[24]
P(VDF-TrFE- CFE)	17.5 vol% BaTiO ₃ nanowires	Ethylenediamine	69	0.09	300	10.48	[95]
P(VDF-HFP)	15 vol% BaTiO ₃ platelets	Polydopamine	20	0.03	175		[96]
PVDF	10 vol% BaTiO ₃ particles	H ₂ O ₂ and DN-101	20	0.05	260	9.01	[97]
PVDF	40 vol% BaTiO ₃ nanoparticles	1-Tetradecylphosphonic acid (TDPA)	48	0.03			[98]
P(VDF-HFP)	50 vol% BaTiO ₃ particles	PFBPA	30	0.03	250	7	[99]
P(VDF-HFP)	50 vol % BaTiO ₃ particles	PHFDA	45	0.02	182.6	6.23	[100]
PVDF	7.5 vol % BaTiO ₃ nanowires	3-aminopropyltriethoxysilane (APS)	24	0.018	230	5.6	[101]
P(VDF-TrFE)	10.8 vol% BaTiO ₃ nanowires	Polydopamine	30	0.02	200		[67]
P(VDF-TrFE)	4.1 vol% Bi ₂ O ₃ -doped Ba _{0.3} Sr _{0.7} TiO ₃ fibers	Polydopamine	16	0,02	227.5	4.72	[102]



Fig. 13. Schematic illustrations of the fabrication procedures of rGo-PU/BN-PU microlaminate composites [37]. Reproduced with permission from American Chemical Society.

explore the dielectric breakdown in polymer composites. In addition, a high throughput simulation based on this model was performed to investigate the effect of microstructure on the breakdown strength, dielectric permittivity and energy density of polymer composites, as shown in Fig. 10. With this model, novel microstructures with desired breakdown strength and energy density can be rationally designed.

The continuous phase-field model can predict the effects of other stimuli on the breakdown behavior, such as mechanical stimulus, thermal stimulus and electric stimulus. By incorporating the phase separation energy, electric energy and gradient energy, a phase-field model was developed to simulate the breakdown strength in polymer nanocomposites, as shown in Fig. 11 [49]. As the thermal energy is not included in this model, an electrothermal breakdown model was developed after including the thermal energy contribution [86]. This electrothermal breakdown model is found to provide good prediction of the breakdown strength for polymer-based nanocomposites with 3D microstructures.

Based on the phase-field model for dielectric breakdown, fillers of high permittivity and elliptic shape or in laminate structure are more effective in resisting the catastrophic damage and avoiding the electric field concentration. A stochastic model has been developed to qualitatively describe the breakdown process [63].

4. Approaches to improve the dielectric permittivity ϵ or breakdown strength $E_{\rm b}$

4.1. Surface functionalization

To design polymer nanocomposite dielectrics, a wide range of filler types are employed, such as nanoparticles (zero dimension), nanofibers (1D) and nanosheets (2D). Fillers are then functionalized to modify their interface properties with the matrix, such as bond strength and dielectric properties, as illustrated in Fig. 12. Several techniques have been reported, including polymer adsorption, polymer coating and grafting to form a non-smooth layer (e.g., star-like polymer as a nanoreactor). In this section, we will focus mainly on conventional ceramic fillers with relatively high dielectric permittivity, such as BaTiO₃ and SrTiO₃ or their doped components. In Table 1, a wide range of surface modifiers were used to improve the dispersion of fillers and their interfacial compatibility with the polymer matrix. Polymer matrix materials including PVDF and P(VDF-HFP) are listed in the table. Surface modifiers, including organic and inorganic compounds have been studied. Also summarized in Table 1 are the consequently improved properties of dielectric permittivity, dielectric loss, breakdown strength and energy density. It is clear that by selecting the appropriate surface modifiers and the ceramic filler content, the desired dielectric property and breakdown strength can be tailored to maximize the energy density in nanocomposite dielectrics.

In addition to improving the interfacial compatibility between the fillers and matrix, surface functionalization can also reduce the agglomeration of fillers in a polymer matrix, thus contributing to the achievement of high dielectric permittivity or breakdown strength. For instance, a novel and efficient method was employed to prepare rGO/PVA porous composites via using PVA as barriers, resulting in a highly conductive network after unidirectional freeze drying [35]. With the PVA serving as a barrier between the aligned conductive networks, this method was found to increase the high dielectric permittivity and to reduce the loss tangent. Moreover, BN-PU acted as a barrier to isolate the conductive rGO-PU layers in microlaminate composites (Fig. 13), achieving a high dielectric permittivity of 1084 and a low dielectric loss of 0.091 [37].



Fig. 14. Methods for achieving high dielectric permittivity polymer nanocomposites via core-shell structure [33]. Reproduced with permission from John Wiley and Sons.

Table 2

Summary core-shell layer and approach used in dielectric composites and their dielectric, breakdown strength, energy density properties.

Polymer matrix	Core-shell	Approach	Dielectric permittivity (1 kHz)	Dielectric loss (1 kHz)	Breakdown strength (kV/mm)	Energy density (J/ cm ³)	References
PVDF	Sheet-like TiO ₂ @BaTiO ₃	Hydrothermal	21	0.05	490	17.6	[103]
PVDF	Nanofiber TiO ₂ @BaTiO ₃	Electrosipinning	16	0.02	360	10.94	[104]
P(VDF-HFP)	Nanowire TiO ₂ @BaTiO ₃	Kinetics-controlled	14.5	0.11	430	9.53	[105]
		coating					
Polytetrafluoroethylene	Nanoparticle TiO ₂ @BaTiO ₃	Sol-gel	240	0.7			[68]
PVDF	Nanoparticle Fe ₃ O ₄ @BaTiO ₃	Chemical	3893	0.9	175	1.8	[106]
		precipitation					
PVDF	Nanoparticle Fe ₃ O ₄ @BaTiO ₃	Chemical	280	0.27			[107]
		precipitation					
PVDF	Nanoparticle Al ₂ O ₃ @BaTiO ₃	Chemical reaction	17.5	0.032	250	4.7	[108]
PVDF	Nanoparticle SiO ₂ @BaTiO ₃	Hydrolysis reaction	12.5	0.03	340	6.28	[109]
P(VDF-HFP)	Nanoparticle	Chemical vapor	1044	17	140	1.1	[76]
	Carbon@BaTiO ₃	deposition					
PVDF	Nanoparticle Ag@BaTiO3	seed-mediated	94.3	0.06			[110]
		growing					
P(VDF-HFP)	Nanofiller	Hydrothermal	15	0.05	360.67	6.4	[84]
	Pt@polydopamine@ BaTiO ₃	reaction					
PVDF	Nanofiber	Coaxial	15	0.03	403.2	14.84	[111]
	TiO ₂ @Al ₂ O ₃ @BaTiO ₃	electrospinning					

4.2. Interfacial design of core-shell structure

It is noted that the large difference in the dielectric permittivity between dielectric fillers and polymer matrix gives rise to localized concentration of the electric field in dielectric composites. To alleviate the mismatch of dielectric permittivity between dielectric filler and polymer matrix, core-shell strategies have been developed to encapsulate the fillers within a core-shell layer with lower dielectric permittivity, as shown in Fig. 14. By engineering the interface between nanoparticles and polymer matrix, core-shell strategies offer the following advantages: (a) Better compatibility with the polymer matrix as the shell can have a more similar chemical structure with the polymer matrix than the high dielectric fillers, thus resulting in homogeneous dispersion of nanoparticles in the matrix; (b) Acting as a buffer layer to minimize the local electric field concentration, realizing the enhanced breakdown strength; (c) Delaying the onset of electrical percolation transition in polymer nanocomposites with electrically conductive fillers; (d) Providing additional flexibility in controlling the critical factors such as the interface thickness, interface interactions and electrical mismatch, as these factors significantly affect the electrical properties of polymer nanocomposites. Table 2 lists a number of core shell examples used as coating buffer layer, including TiO₂, Fe₃O₄, Al₂O₃, SiO₂, C, Ag and Pt. The core-shell layer typically has a dielectric permittivity value between those of the dielectric filler and the polymer matrix. From the resulting dielectric permittivity, dielectric loss, breakdown strength listed in Table 2, it is clear that the core-shell design significantly improved the energy density compared with their pristine structures reported in composite materials.



Fig. 15. Schematic diagram for illustrating the fabrication of topological films via layer by layer casting. BTO-np stands for BaTiO₃ nanoparticles, BTO-nf stands for BaTiO₃ nanofibres [38]. Reproduced with permission from John Wiley and Sons.



Fig. 16. Schematic diagram illustrating the preparation of the topological-structure polymer nanocomposites [39]. G layer stands for PVDF mixed with graphene oxide nanosheets coated with TiO₂ nanoparticles (GT), while B layer is PVDF mixed with Ba_{0.6}Sr_{0.4}TiO₃ nanofibres Reproduced with permission from Elsevier.



Fig. 17. Distribution of electric field strength and polarization simulated by phase-field model for polymer nanocomposites with different designed structures [39]. Reproduced with permission from Elsevier.

4.3. Structural design

4.3.1. Topological structure

It is generally acknowledged that the high dielectric permittivity is usually achieved by sacrificing the breakdown strength, which substantially limits the improvement of energy density. Conventional nanocomposites made by embedding zero-dimensional nanoparticles into a polymer matrix [112] can suffer significant reduction in the breakdown strength caused by the local electric field concentration when dielectric permittivity of the filler far exceeds that of the polymer matrix.

Substantial effort has been devoted to reducing the local electric field concentration, including the techniques of surface functionalization and core-shell structure design as discussed in Section 3.1 and 3.2. To further address this challenge, a typical 3-layer structure (Fig. 15) was developed by using central layer of high breakdown strength and outer layers

of large dielectric permittivity. This kind of interleave composite structure has been demonstrated to simultaneously achieve high dielectric permittivity and breakdown strength [38]. More interestingly, the developed reversed structures of BGB and GBG (Fig. 16) based on a typical 3-layer BGB structure resulted in a consistently higher breakdown strength as a function of the filler content (graphene oxide nanosheets coated with TiO2 nanoparticles) compared to that of GBG structure [39]. Other laminar nanocomposites with three layers including PVDF/BNNS as the outer layers and PVDF/BST as center layer were fabricated, displaying a high energy density of 20.5 J/cm^3 and a high breakdown strength of 588 kV/mm (where BNNS stands for the boron nitride nanosheets and BST stands for the barium strontium titanate). Comparing with the property of commercial biaxially oriented polypropylene, this kind of laminar nanocomposites showed superior power density and provide a new route for designing composite dielectrics with high performance [113].



Fig. 18. (a) TEM image, (b) zoom-in image of (a) and (c) schematic of core double shell structured $Al_2O_3@TiO_2@BaTiO_3/PVDF$ nanocomposites; (d)–(f) Finite element analysis of distribution of electron potential, electric field and current density of $Al_2O_3@TiO_2@BaTiO_3/PVDF$ nanocomposites [111]. Reproduced with permission from Royal Society of Chemistry.



Fig. 19. Schematic illustration of (a) series model of capacitors; (b) electric field distribution; (c) dielectric breakdown strength model; (d) leakage current distributed in polymer composite with multilayers based on finite element simulation [116]. Reproduced with permission from Royal Society of Chemistry.

Finite element simulation was also performed on the evolution of breakdown strength process, and the results reveal the local electric field distribution in the laminated nanocomposites [50]. Owing to this specially designed topological structure, electric field at the layer interfaces was much lower than within the adjacent layers, preventing the further penetration of electrical treeing process and promoting the enhancement of breakdown strength. Reverse configurations were designed by swapping the high breakdown strength layer with the high dielectric permittivity layer. Results of finite element analysis (Fig. 17) and experimental results show that the local electric field of high

dielectric permittivity layer decreases while the electric field increases, resulting in high breakdown strength layer. Therefore, modifying the electric field distribution by tuning the topological structure of nano-composites [39,112] is an attractive technique to enhance the performance of dielectrics.

4.3.2. Multilayered structures with hierarchical interfaces

The dielectric permittivity mismatch between fillers and polymer matrix is key factor hindering progress towards achieving high energy density. This mismatch in dielectric permittivity causes localized



Fig. 20. Recent advances in flexible polymer composite dielectrics: (a) Gate dielectrics for flexible electronics [118]; reproduced with permission from American Chemical Society. (b) Transparent and self-healing dielectrics for low-field-emission flexible optoelectronics [130]; reproduced with permission from Nature Publishing Group. (c) Inkjet-printed flexible low-voltage synaptic transistor array [131]; reproduced with permission from Nature Publishing Group. (d) Stretchable organic electronics by integrating elastomer matrix and organic semiconducting polymer [132]; reproduced with permission from The Royal Society of Chemistry. (e) Electronics of hyper-stretchable elastic composite dielectrics for energy harvesting [133]; reproduced with permission from John Wiley and Sons.

concentration of electric field and hence decreases the breakdown strength. As a result, the interfacial barrier effect becomes significant when increasing the filler content in nanocomposite dielectrics. Moreover, the filler aggregation occurs when a high filler loading is added to a polymer matrix. The fillers may come into contact with each other and form the conductive path for charge carriers, resulting in a degraded breakdown strength. Therefore, the optimum filler content in conjunction with designed layered structure [114] or gradient structure [115] is required to maintain the electric field distribution capable of being electrical insulation and thus contribute to the enhancement of energy storage.

Recent advances reveal that the core-shell or core-multi-shell design of materials are a promising way to resolve the conundrum between dielectric permittivity and breakdown strength [111]. In Fig. 18(a)-(c), double core-shell structure BaTiO₃@TiO₂@Al₂O₃ was prepared via a novel coaxial electrospinning approach, showing an improved breakdown strength and energy density. Moreover, this kind of nanocomposites showed superior discharge rate of 0.37 µs. [111]. Simulation



Fig. 21. A schematic to show the machine learning strategy [142]. Reproduced with permission from Nature Publishing Group.

was performed to explain the enhanced breakdown strength. Fig. 18(d)–(f) shows the electron potential, electric field and current density of Al_2O_3 @TiO_2@BaTiO_3/PVDF nanocomposites. Compared with that of pristine BaTiO_3/PVDF nanocomposites, the new design achieved decreased electron potential in Fig. 18(d), homogeneously distributed electric field in Fig. 18(e), and low local electric current density in Fig. 18(f).

Dielectric materials with multilayers can be viewed as series circuit of capacitors after applying an electric field (Fig. 19). As the electric displacement exists at the interface of adjacent layers, the electric field in each layer will be affected by the different permittivity of each layer.

When taking two layered composites as an example, the electric displacement can be expressed as: $D = \varepsilon_1 E_1 = \varepsilon_2 E_2$. If the constant voltage V is applied, local electric field in each layer can be determined based on series model [116]: $E_1 = \frac{V}{d_1 + \frac{r_1}{c_2} d_2}$ and $E_2 = \frac{V}{d_2 + \frac{r_2}{c_1} d_1}$, where d_1 and d_2 represent the thickness of each layer. The layer with lower permittivity will gain a higher proportion of the redistributed electric field, protecting the layer with higher permittivity from the high applied electric field [38,117]. Therefore, layered polymer nanocomposites can achieve high breakdown strength compared with that of single layer counterparts.

5. Recent progress in flexible and stretchable polymer composite dielectrics

Flexible and stretchable polymer composite dielectrics nowadays have been attracting tremendous attention owing to their high dielectric strength and excellent flexibility [118,119]. To meet with the increasing demands of electronics, flexible polymer composite dielectrics with desired properties are proposed to have high breakdown strength, superior dielectric permittivity, excellent energy density and promising mechanical property [120].

Instead of the rigid fillers being incorporated into polymer matrix, liquid-metal microdroplets [121] are dispersed into hyperelastic materials with high dielectric permittivity to achieve the exceptional electro-elasto properties. By integrating dielectric polymer with novel ceramic particles, high performance flexible organic field-effect transistors are fabricated based on polymer-ceramic dielectric composites [122], offering a great potential in designing the portable organic electronics. In addition, low-voltage-driven field-effect transistors are developed by binary polymer composite dielectrics consisting of PVDF-HFP/PVP [123] or PAA/PMMA [124], where flexible electronics devices can be operated under both deformation and low voltage stimuli.

Organic soft electronics are aiming for human-friendly electronic applications, where stretchable polymer gate dielectric [125] in combination with segmented elastomeric network structure is used for specific stretchable organic transistors [126]. By modifying the network structure of hybrid dielectric film with Zirconia, thin-film transistors with good mechanical stretchability are fabricated [127]. The fully inkjet printed capacitors consisting of ceramics/polymer composite dielectric materials are developed in flexible substrate [128]. After controlling the geometry of metal particle in elastomer matrix, either a parallel-plate capacitor with stable capacitance or cylindrical fiber strain sensor can be developed, showing their significant potential in flexible electronics [129].

Recent progress in flexible polymer composite dielectrics have revealed their advances in the application of flexible electronics. High dielectric permittivity dielectrics (Fig. 20(a)) followed by both material concept design and fabrication technique are emerging as dielectric gates, where flexible electronics, such as the fabricated thin film transistors with desired mechanical deformation and dielectric property [118]. However, dielectric materials with desired dielectric permittivity



Fig. 22. Digital images of (a) P(VDF-HFP) film; (b) nanocomposites with BaTiO₃ nanospheres; (c) BaTiO₃ nanofibers. (d) Cycle performance of nanocomposite films with BaTiO₃ nanofibers from areas $1 \times 1 \text{cm}^2$ to $10 \times 10 \text{ cm}^2$ [23]. Reproduced with permission from John Wiley and Sons.

remains to be explored to improve the performance and environmental stability in flexible electronics. To further promote the development of electronic skins in wearable electronics and soft robots. low-field-emission flexible optoelectronics (Fig. 20(b)) with transparent, mechanical stretchable and self-healing dielectrics are developed [130]. Moreover, the dielectrics in optoelectronics can be stretched up to 20%, showing its good elasticity. To enable the smooth interaction between flexible electronics and human body, low-voltage synaptic transistor arrays (Fig. 20(c)) are fabricated through Inkjet-printed technique [131], where synaptic behaviour of neurons can be mimicked. Based on this kind of bioelectronics, the development of human-machine interfacing/interaction will be substantially promoted. Fig. 20(d) shows stretchable organic electronics achieved by integrating elastomer matrix and organic semiconducting polymer [132], where the designed flexible electronics enable irregular interfaces interacting with soft tissues. By controlling the morphology of dielectric materials with specific approaches, improved stretchability with the reduced external energy in electronics can be realized. To compensate the lacked power energy in functioning flexible electronics, high-output energy conversion devices are required. Fig. 20(e) shows flexible electronics made by hyper-stretchable elastic composite dielectrics for energy harvesting [133], where power supply can be achieved owing to the capability of generating or collecting energy for composites after experiencing a certain stimulus.

Therefore, polymer composite dielectrics will inevitably advance the design of flexible electronics in either skin electronics or medical devices. However, it should be noted that the modulus mismatch between various materials in nanostructured composites requires more efforts in reducing this kind of discrepancy. On the other hand, to well integrate nanomaterials into polymer matrix, the homogeneity and structural stability in composites also need special attention when performing the experimental design.

6. Machine learning

To accelerate the use of composite dielectrics into practical

applications, a predictive design tool is urgently needed [134]. Computational approaches have also been applied to guide the design of polymer composite dielectrics, such as density functional theory, molecular dynamic simulations and machine learning strategy [135]. By exploiting machine learning techniques, a "Materials Genomics" approach based on quantitative structure property relationship was developed and used to predict the thermomechanical property of polymer composites, consequently realizing the virtual design of novel materials [136]. With the advances in materials genome initiatives, rapid prediction based on the past data instead of direct experiments have promoted the machine learning models [137]. The data-driven materials informatics are starting to undertake a new role, shaping the conventional materials science [138].

Strategies for designing polymer composite dielectrics include processes such as computation guidance, experimentation and machine learning. Based on sufficient data, a genetic algorithm combined with learning models was able to design materials with desired properties so that the problems of choosing materials with desired properties can be quickly resolved [139]. On the other hand, to efficiently obtain quantitative property predicted models, machine learning in conjunction with simulations can also be very effective [140]. The recent success in obtaining high energy density for polymer composite dielectrics has been achieved through a co-design paradigm [141].

A comprehensive phase-field model in conjunction with machine learning was exploited to study the electric, thermal and mechanical properties in polymer dielectrics [142]. The machine learning strategy is shown in a schematic in Fig. 21. As machine learning is recognised as a useful tool, the modeling and design of composites materials based on various types of machine learning algorithms have also been attempted to optimize the composites [134]. In summary, the machine learning technique is envisioned to improve the optimize the design of materials with novel and unprecedented properties.

However, all these theories cannot quantitatively describe the specific process of electric field distribution and breakdown, although much progress has been achieved in polymer nanocomposite dielectrics for energy storage.

7. Potential applications for scale-up production

Dielectric capacitors utilize their inherent high-power density, i.e., fast energy uptake and delivery, thus enabling them to be used in high performance power electronics or in high pulsed-power applications. The stored energy was delivered in 10^{-6} to 10^{-3} s for pulse-discharge applications [143]. Specific applications can be delivered to the following aspects: inverters of electric (an apparatus converting DC to AC), medical devices including defibrillators, surgical lasers. Implantable cardioverter defibrillators are typically planted in the chest to measure heart electrical signal and deliver one or more electric shocks ranging from a few microjoules to powerful shocks of 25–40 J in about 5–10 s [144]. Modern defibrillators capacitors require energy density over 5 J/cm³ [145]. Other applications include electrical vehicles, pulsed weapons systems and power electronics.

High discharge efficiency has been a challenge in the polymer nanocomposite system, especially for the large-scale production, as the pore, void and microstructural weak areas will easily arise under the large-scale fabrication. In Fig. 22, large scale production of nano-structure composites films was prepared by regulating nanoparticles to construct anisotropic nanostructures. The size of this film nano-composites can reach 25×25 cm. Energy density of 25.5 J/cm^3 with a discharged efficiency of 76.3% was obtained, showing a relatively high energy density and discharge efficiency for this large scale produced nanocomposite films [23]. In addition to this, the roll-to-roll processing for large scale products can be achieved based on this developed technique, which opens the avenue for realizing the practical application. In addition to the polymer nanocomposite dielectrics used in room temperature, the scalable polymer dielectrics targeting at elevated



Fig. 23. Summary of (a) dielectric permittivity versus breakdown strength versus energy density in 3D plot and (b) energy density in recently reported results of literature.

temperature is also required to meet the increasingly demands under extreme conditions [146].

8. Challenges and summary

To compare with current energy storage techniques of batteries, supercapacitors and fuel cells, dielectric capacitors have been attracting considerable attention owing to their high-power density with fast charge and discharge rate. The prevalent application of dielectric capacitors has been hindered by their low dielectric permittivity, low breakdown strength, poor mechanical flexibility and low energy density [147]. To overcome these shortcomings, incorporating ceramic filler into polymer matrix offers a desired solution to prepare polymer based dielectric composites [148]. For the future development of polymer nanocomposite dielectric for energy storage, by embedding 1D [148] or 2D ceramic nanofillers [149,150] into polymer matrix to fabricate the nanocomposites, a considerable high energy density with high dielectric permittivity can be achieved owing to the nanofillers capable of producing large dipole moments. After implementing structure engineering technique in nanofillers, such as surface functionalization and structure alignment, the fabricated polymer nanocomposites are proposing to achieve large dielectric breakdown strength and pronounced improvement of energy density. For instance, by alternatingly stacking 2D boron nitride nanosheets and reduced graphene oxide, the fabricated micro-sandwich composites show a high thermal conductivity (1.49 W/m·K) and a high energy density (14.2 J/cm³) owing to their synergistic effect of fillers in combination with the architecture design [150]. By integrating ionic liquid and nano-montmorillonite with PVDF, nanocomposites exhibit superior energy storage performance, showing the energy density of 12.8 J/ cm^3 with a charge-discharge efficiency over 80% [151]. In addition, to construct composite dielectrics with both high energy density and high efficiency, hybrid polymer composite dielectric films are prepared with energy density of 22.06 J/cm³ and efficiency of 72% [152], while bilayer ferroelectric/linear films are compared and only show the discharge energy density up to 9.6 J/cm³ with an efficiency of 58% [153]. Interestingly, a remarkable high energy density up to 30.15 J/cm³ with an efficiency of 78% is achieved in multilayer polymer nanocomposite dielectrics owing to their synergistic effect of micro-/mesoscopic interfaces in nanocomposites, especially the contribution of dielectric/dielectric interfaces. By introducing the dielectric/dielectric interfaces into multilayer structured nanocomposites, enhanced polarization and breakdown strength will be harvested, contributing to a high energy density [154]. Ferroelectric PVDF and its copolymers are studied to verify the dielectric/dielectric interface design owing to their respective high breakdown strength. After

exploiting the sandwich structure with the aligned fillers, PVDF based nanocomposites can achieve the energy density up to 20 J/cm³ with the efficiency over 70% [155]. Therefore, to achieve both high energy density and high charge-discharge efficiency of polymer nanocomposites dielectrics, structural engineering such as surface functionalization in either ceramic fillers or structural aligned fillers, in combination with heterostructures or sandwich structures or topological structures are employed to prepare polymer nanocomposite dielectrics. Furthermore, the internal stress in polar nanostructured relaxor ferroelectrics can be engineered to achieve a pronounced improvement of energy density up to 39.8 J/cm³ [156]. In addition, with the increasing demands of composite dielectric for certain extreme surroundings, high temperature dielectrics are also worthwhile to be explored, which can be targeted at the nanostructured dielectric materials in either bulk ceramics or thin films.

On the other hand, combining the merits of high breakdown strength of polymer and the high dielectric constant of ceramics nanoparticles, polymer nanocomposite dielectrics have becoming promising in energy storage during the past few years. To date, the incredible progress and breakthrough have been achieved in the fabrication of polymer nanocomposites. However, a number of critical problems limiting the practical applications, such as the low energy density, charging-discharging time, flexibility and stability has to be addressed. The experimental and theoretical understandings on the relationship between structures and functionalities of polymer nanocomposites have been recently studied. The review summarized recent achievements related to polymer nanocomposite dielectrics for energy storage, and the dielectric permittivity versus breakdown strength in recently reported results of literatures was also shown in Fig. 23 to indicate the current state of art in this research field. However, there is a large gap for development of polymer nanocomposite dielectrics into realizing the practical energy storage applications in the future.

There are still some problems remaining to be solved: (a) the conundrum between attaining high dielectric permittivity and high breakdown strength; (b) mismatch of dielectric permittivity between filler and matrix. Promising solutions are put forward as follows: (a) comprehensive understanding of dominant influence of filler-matrix interface; (b) structural engineering including both modifying the interface between filler and matrix and constructing novel interface structures. (c) Modelling and machine learning to achieve the optimized properties of dielectric permittivity and breakdown strength.

Moreover, achieving high discharge efficiency has been a challenge in the polymer nanocomposite system. New approaches to mitigate the interfacial polarization are needed. For instance, the composition and local structure of polymer composites should be carefully tailored to minimize the impact of interfacial polarization. Substantial efforts should be placed on designing the effective storage devices, such as engineering the structure via using multilayer technique, series and parallel connecting. Consequently, instead of the current P-E dynamic and DC static method, alternative methods for performance evaluation are needed. The fabrication and characterization technique of polymer nanocomposite dielectrics here will not only open up new opportunities for fundamental material research, but also inspire innovations for designing high energy-density storage devices.

Despite recent advances in ultrahigh power density, high voltage endurance and desired reliability in electrostatic capacitors, the substantial increase in energy density has been hindered by the sacrificed polarization. To resolve this problem, nanoscale domain manipulation strategy in conjunction with phase-field model can be applied to successfully improve the whole energy storage performance by suppressing the hysteresis to achieve the reduced energy loss. In this context, leadfree BiFeO₃-BaTiO₃-SrTiO₃ films have been prepared to achieve the nanodomains with both rhombohedral and tetragonal phases in a cubic matrix, subsequently achieving a high polarization and a high energy density of 112 J/cm² owing to the achieved diminished hysteresis. In addition, this system features a high energy efficiency of about 80%. By using this strategy, it enables the design of high performance dielectrics based on the modulation of nanoscale domain structure, which also paves a way for designing other similar system of function materials [21]. The long-range ferroelectric (FE) order was broken into nanodomains, which was represented the typical examples of [157] BaTiO₃-BaZrO₃ and [158] BiFeO₃-SrTiO₃. Relaxor ferroelectrics (RFEs) shows a delayed polarization, where maximum polarization will not be achieved until the filed reaches breakdown strength, showing a promising way for enhancing energy density. In addition to this, suppressed hysteresis is shown in RFEs with low energy loss, contributing to a high energy efficiency.

Therefore, the desired dielectrics are to endow with the following advantages: (a) high flexibility, (b) high dielectric constant, (c) low dissipation factor, (d) high thermal stability, (e) simple processability and (f) good dielectric properties. New insights into the unique properties of the nanoparticle filler, filler modification and the dispersion between filler and polymer matrix are anticipated for the future research. In addition, to meet the practical applications at extreme conditions, such as aerospace power systems and underground oil industries, the exploration of polymer composite dielectrics with remarkable energy density and excellent thermal stability at elevated temperatures is also crucial.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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