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REVIEW ARTICLE

Review of recent advances of polymer based dielectrics for high-energy storage in electronic power devices from the perspective of target applications

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Abstract Polymer-based dielectric capacitors are widely-used energy storage devices. However, although the functions of dielectrics in applications like high-voltage direct current transmission projects, distributed energy systems, high-power pulse systems and new energy electric vehicles are similar, their requirements can be quite different. Low electric loss is a critical prerequisite for capacitors for electric grids, while high-temperature stability is an essential pre-requirement for those in electric vehicles. This paper reviews recent advances in this area, and categorizes dielectrics in terms of their foremost properties related to their target applications. Requirements for polymer-based dielectrics in various power electronic equipment are emphasized, including high energy storage density, low dissipation, high working temperature and fast-response time. This paper considers innovations including chemical structure modification, composite fabrication and structure re-design, and the enhancements to material performances achieved. The advantages and limitations of these methods are also discussed.

Keywords dielectric capacitors, polymer-based dielectrics, energy density, dielectric loss, working temperature, frequency response

1 Introduction

Sustainable development based on clean energy has become a major research field during recent decades, which in turn has witnessed a growing body of evidence of manmade climate change. Sustainable development concerns the generation and storing of energy in environmentally friendly ways, as well as improving the efficiency of conversion into electric energy for further usage. Nowadays, the growing diversification of new clean power sources [1,2] and rapidly increasing power generation are factors driving the transformation of centralized electrical grids into distributed structures. There is a growing need for more efficient energy conversion and storage facilities, which collect and merge the scattered electric power into the main grid system. Researchers and engineers have investigated potential avenues for improving the large-scale energy conversion process in terms of high energy density, high efficiency and long-term reliability, and to this end have developed numerous devices including electrochemical batteries [3–5], supercapacitors [6,7], hydrogen storage [8–10] and dielectric capacitors.

Dielectric capacitors are widely used in high-voltage direct current (HVDC) transmission systems [11], electric vehicles [12] and pulse power systems [13], owing to their fast charge-discharge speeds, low manufacturing costs, high reliability, and good operating safety [14]. Dielectric capacitors, which were invented back in the 1970s, now account for more than 70% of capacitor production [15]. As a functional component, the performance of a dielectric capacitor is determined by its dielectric material properties. Numerous materials, including ceramics, mica, paper, electrolyte and synthetic polymers, have been used for making dielectric capacitors. Among them, polymer-based materials are most extensively used because of their good electrical properties, low cost, admirable processability and high flexibility. However, conventional polymers like polypropylene have small dielectric constant and low heat distortion temperature, leading to low energy storage density and working temperature, which are inappropriate for smart grids and electric automobiles.

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Research into improving energy storage performances of polymer dielectrics have been reported and summarized in several reviews [16–19]. As a critical aspect of performance relating to all power electronic devices, energy storage density in relation to numerous material species has been widely discussed. It is the fundamental requirement, albeit not the sole property of polymer dielectrics, which must be considered in specific applications. A good example is biaxially-oriented polypropylene (BOPP), which has a relatively low energy storage density, but which remains the most widely used thin film dielectric capacitors for power grids. This is because, for practical applications, for power grids greater concern is given to dielectric loss compared to energy storage density, when considering long-term reliability. As indicated in Fig. 1, other performance aspects are a priority in other applications, e.g., fast frequency response is needed for laser weapons, and high temperature stability is a prerequisite for electric vehicles. In a number of applications, properties other than energy storage density are of greater importance.

Starting from the basic principle of physical energy storage by dielectrics polarization, this review paper summarizes the range of polymer-based dielectrics from the perspective of requirements, and in view of target applications including electrical power systems and electronic devices. Methods for enhancing energy density, dielectric strength, service temperature, frequency response and confining dielectric loss are highlighted, and illustrated where appropriate. Advantages and disadvantages of the performance properties of different forms of dielectrics are also discussed in order to facilitate understanding of their appropriate application areas and their limitations.

2 Basic principles of energy storage

Energy storage in polymeric media is essentially a polarization process. When an electric field is applied to a dielectric device, the dipoles inside become oriented. This orientation can be achieved in many ways. Depending on the scale of polarization structures in polymers, there could be polarization of electron clouds, bonds vibration, or movement of end-groups and molecular segments, etc. These polarized structures respond to external electric fields at various frequencies. Figure 2 shows five typical polarization modes, including electronic polarization, atomic polarization, ionic polarization, dipolar polarization and interfacial polarization [20,21]. In order to create a larger polarization structure, more energy is needed to drive the necessary molecular motivation, and so there is a lower frequency range.

In providing a basic model of polarization, Eq. (1) defines polarization intensity P as follows [22];

$$P = \varepsilon_0 \chi E, \tag{1}$$

whereby $\varepsilon_0 = 8.85\times10^{-12}$ F·m^{-1}, and represents the vacuum dielectric constant; E is the electric field being applied to the dielectrics; and χ is the dielectric polarization, which is an inherent property of the dielectric materials. In order to express the scale of electrical displacement, Eq. (1) is combined with the Gauss theorem in order to form Eq. (2) [23]:

$$D = \varepsilon_0 E + P = \varepsilon_0(E + \chi E) = \varepsilon_0(1+\chi)E = \varepsilon_0\varepsilon_r E, \tag{2}$$

whereby D represents the electrical displacement, and ε_r is the relative dielectric constant of the polymer.

The charging and discharging processes of the polariza-

Fig. 1 Application of dielectric capacitors in various fields, including HVDC projects, distributed energy networks, new energy vehicles, laser weapons and pulse power systems.

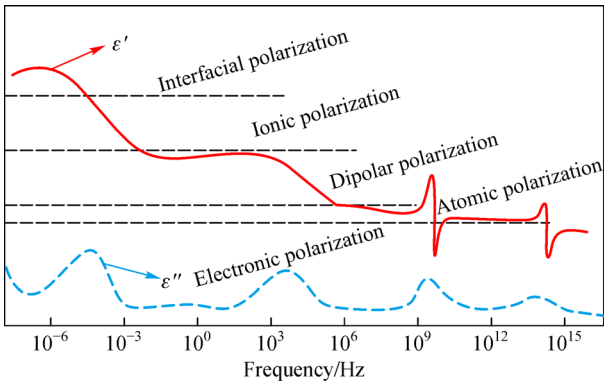


Fig. 2 Different types of polarization of frequency in polymers, adapted from [21]. NB ε' denotes dielectric constant and ε'' denotes dielectric loss.

tion and depolarization of dipoles inside the energy storage media are microscopic in nature. When an electric field is applied, the internal structure of the polymer can rebalance from its original equilibrium state to another one with higher potential energy. This enables the energy from the outside power source to be temporarily "stored" in the media. When external electric field E is excluded, the structures of the dipole moment inside the material gradually recover to their original states to different extents. This discharge process can be observed in external circuits. Figure 3 shows three typical charge-discharge modes of polymers, which are represented by displacement-electric field (D-E) curves. A charging line (black solid line) and a discharging line (red solid line) can be found in each D-E curve.

When an alternating current (AC) electric field is applied to both sides of the lamellate material, it shifts and stretches the dipole structures. The amplitude of their motion changes is determined by the magnitude of the externally applied electric field. When the applied electric field is small, the magnitude of the dipole displacement, whose amplitude remains linear with the electric field magnitude, is slight. Such dipole displacement can easily return to its original position when the external electric field is removed. Typically, such an electric field on polymer film is lower than 200 MV·m^{-1} [24].

However, when the external field increases (Fig. 3(b)), a greater electric force field drives the dipole movement to an irreversible range beyond the linear range, so that, even if the electric field is removed, the dipole structure inside the polymer cannot completely return to the original state. A portion of the residual displacement can be observed when the electric field is removed. Figure 3(c) shows the D-E curve of a ferroelectric polymer with a large amount of a certain crystalline phase, which is different from the amorphous or low crystallinity polymers described above. The ferroelectric material exhibits broad hysteresis loops with large remnant polarization due to the presence of ferroelectric domains [25–27]. An additional extra electric field needs to be provided in order to counteract the effects of the remnant displacement. However, it should be emphasized that the applied electric field should not excess the material's breakdown strength (E_b), otherwise the material is destroyed and loses its energy storage capability.

For energy storage films, an efficiency of 100% cannot be sustained under a high electric field, thus it is crucial to quantify the charge-discharge energy and define the efficiency. The energy density of dielectric materials can be calculated using Eq. (3) (as indicated in the blue area in Fig. 3) [28]:

$$W = \int E\mathrm{d}D. \tag{3}$$

When the dielectrics are linear materials (Fig. 3(b)), Eq. (3) can be simplified as follows [29]:

$$W = \int E\mathrm{d}D = \frac{1}{2}\varepsilon_0\varepsilon_r E^2. \tag{4}$$

Although high energy density can be obtained by charging with a high electric field, the energy loss increases, and that is accompanied with current leakage from the material, leading to lower energy storage

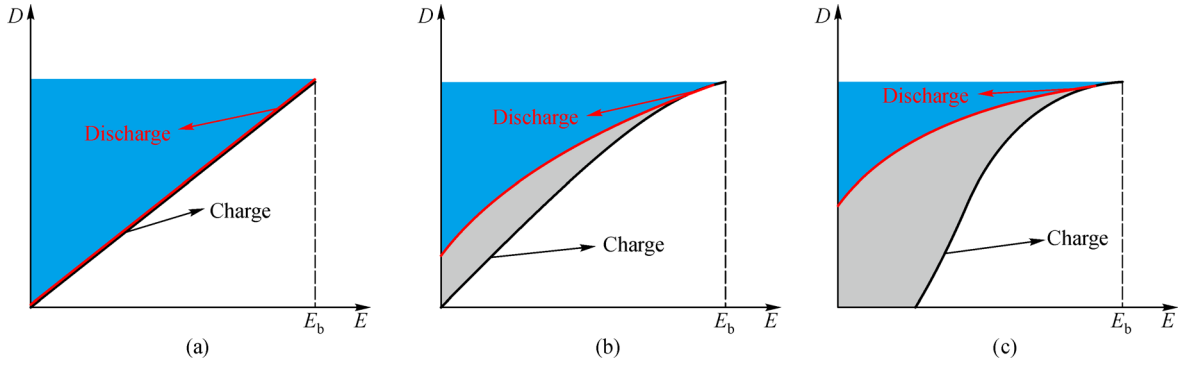


Fig. 3 Schematic illustrations of the three typical D-E curves. The black line and the red line show the charge and discharge pathway, respectively. The blue area and grey area represent charging energy density and loss energy density, respectively. E_b is the breakdown field strength of dielectrics materials.

efficiency. In practical applications, the energy storage efficiency of the material is as important as its energy storage density. The energy storage efficiency can be defined as the ratio of the discharge energy storage density to the charge energy storage density:

$$\eta = \frac{W_d}{W_e}, \quad (5)$$

whereby W_e is the charging energy density, and W_d is the discharge energy density. Increasing the energy storage efficiency of the dielectrics leads usually to less energy loss and better reliability.

3 Methods for increasing energy storage density in film capacitors

Energy storage density is the core parameter for all standards for estimating the performance of energy storage materials. According to the energy density equations presented in Section 2, the energy storage density of polymer-based materials can be improved by (1) increasing the dielectric constant and (2) enhancing the field strength of the materials.

3.1 Increasing the dielectric constant

The most commercially viable dielectric material for capacitors is BOPP. However, the energy storage density of BOPP is only 10 $J \cdot cm^{-3}$ due to its low dielectric constant (2.2 at 1 kHz). Increasing the dielectric constant of polymers is an effective way to develop high-energy storage density materials. Polymer polarity enhancement and organic-inorganic hybridization are the two main methods.

3.1.1 Polymer polarity enhancement

Ferroelectric polymers composed of polyvinylidene fluoride (PVDF) have a high dielectric constant (around 10 at 1 kHz) due to their inherently strong polar C−F bonds and dipolar spontaneous polarization [30]. The large electronegativity difference between the carbon and fluorine atoms causes the C−F bond to possess a strong dipole moment of 6.4×10^{-30} C·m, which constitutes a high polarity base unit [31]. PVDF is a polymer that can be crystallized to include different crystal phases (such as α-, β-, γ-, δ-, etc.) [32], and which has a crystallinity of 50% to 60%. To further increase the dielectric constant of PVDF, researchers have produced a series of PVDF-based binary copolymers via copolymerization of inylidene fluoride with trifluoroethylene (TrFE) [33,34], chlorotrifluoroethylene (CTFE) [35], hexafluoropropylene (HFP) [36] and bromotrifluoroethylene (BTFE) [37]. PVDF-based binary copolymers with higher dielectric constant, including P(VDF-TrFE) (18 at 1 kHz), P(VDF-CTFE) (13 at 1 kHz), P(VDF-HFP) (5.6 at 1 kHz) and P(VDF-BTFE), have been generated. Among them, P(VDF-TrFE) exhibits the characteristics of ferroelectric polymers under the effects of electron irradiation [38]. Moreover, introducing a third part (polymer) can further enhance the dielectric constant of the materials. According to a number of previous studies, materials including fluorovinyl chloride (CFE) [39,40] and CTFE [41,42] can be introduced into the P(VDF-TrFE) binary copolymer in order to yield ternary copolymers with a higher dielectric constant, such as P(VDF-TrFE-CFE) (55 at 1 kHz) and P(VDF-TrFE-CTFE) (47 at 1 kHz). Table 1 shows the structural formula of PVDF-based polymers, binary copolymers and ternary copolymers.

Dielectric properties can also be effectively improved by introducing a highly polarized group into the polymers, such as sulfone [43], hydroxyl [44,45] and cyano [46]. Thakur et al. introduced a hydroxyl group into PVDF using radiation-induced grafting of 2-hydroxyethyl methacrylate (Fig. 4). Their results showed that the dielectric constant (>40 at 1 kHz) was about 4.5 times higher, compared to pure PVDF at room temperature [44]. Similarly, Li et al. used atomic-transfer radical polymerization to attach hydroxyethyl methacrylate to P(VDF-TrFE-CTFE) (Fig. 4), which can reduce the crystal size of the polymers and weaken the ferroelectric effect of the polymer, thereby improving the energy storage (14 $J \cdot cm^{-3}$) of the system [45]. Other polymer species have also been selected for

Table 1 Structural formula of PVDF-based polymers, binary copolymers and ternary copolymers

Material	$-[X]_m-[Y]_n-[Z]_p-$		
	−X−	−Y−	−Z−
PVDF	$-CH_2-CF_2-$	−	−
P(VDF-TrFE)	$-CH_2-CF_2-$	$-CH_2-CHF-$	−
P(VDF-HFP)	$-CH_2-CF_2-$	$-CH_2-C(CH_3)F-$	−
P(VDF-BTFE)	$-CH_2-CF_2-$	$-CH_2-CFBr-$	−
P(VDF-CTFE)	$-CH_2-CF_2-$	$-CH_2-CFCl-$	−
P(VDF-TrFE-CTFE)	$-CH_2-CF_2-$	$-CH_2-CHF-$	$-CF_2-CFCl-$
P(VDF-TrFE-CFE)	$-CH_2-CF_2-$	$-CH_2-CHF-$	$-CH_2-CFCl-$

modification. One example is cyano-substituted polycarbonate (Fig. 4), which has a higher dielectric constant than polycarbonate (PC) [46].

3.1.2 Organic-inorganic hybridization

Organic-inorganic hybridization is another effective means of improving the energy storage density of polymer-based dielectrics. This involves introducing ceramic materials, each with a high dielectric constant, like $BaTiO_3$ (BT) [47,48], $BaSrTiO_3$ [49,50], $SrTiO_3$ [51], TiO_2 [52], etc. These ceramics are filled into the polymer matrix, and the dielectric constant of the resulting composite materials is closely related to that of the components in the system. It has been shown in some previous studies that the type, size [53] and distribution [54] of the fillers have diverse effects on the dielectric constant. The dielectric constant of the composite system can be calculated by utilizing corresponding mathematical models so as to yield an optimal composite design. However, it has been demonstrated via intensive experimentation that a considerable amount of inorganic fillers are generally required in order to obtain a considerable high dielectric constant. For example, Bai et al. [55] developed a ceramic-filled polymer based material with a dielectric constant of 100, with filler content of around 40%. High-dielectric constant ceramics such as ferroelectric ceramics added to the polymers, which can greatly increase the dielectric constant and thus lower the required ceramic content in the resulting composite. Wang et al. [56] used $Na_{0.35\%}Ba_{99.65\%}$-$Ti_{99.65\%}Nb_{0.35\%}O_3$ (NNBT) as filler to prepare ceramic-polymer composites using PVDF as matrix. Their results showed that PVDF-0.5NNBT has a high dielectric constant (more than 100 at 1 kHz) and low dielectric loss (about 0.037 at 1 kHz) at a filler amount of 10 vol-%. The relevant information is summarized in Table 2.

Another way to develop high-dielectric constant composites by obtaining materials with high energy density is to add conductive or semi-conductive particles to the polymer in order to form a percolation system [57,58], such as filling PVDF, P(VDF-TFE) and P(VDF-CTFE) with metal nanoparticles like Ni [59], Ag [60] and TiO_2 monolayers (TOMLs) [61]. Specifically, Wen et al. [61] firstly filled PVDF with a small amount (1 wt-%) of TOMLs as fillers to obtain dielectric composites with a dielectric constant of 12 at 1 kHz and an energy density of 21.1 $J \cdot cm^{-3}$. The percentage of introduced filler in the composite is substantially smaller than that of many other

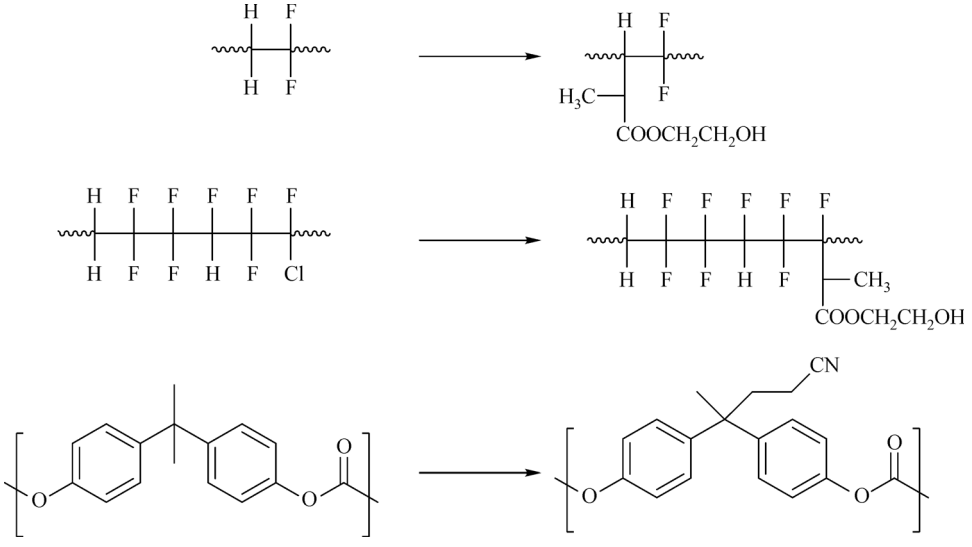


Fig. 4 Chemical structures of the pristine polymers before and after modification.

Table 2 Volume fractions of some typical ceramic fillers for improving the dielectric constant of composites, and the dielectric constants of the composites

Ceramic fillers	Polymer	$\varepsilon^{a)}$	Filler/vol-%	$\varepsilon^{b)}$	Energy storage density/($J \cdot cm^{-3}$)	Ref.
BT	P(VDF-HFP)	~5	30	~20	9.7	[47]
$BaSrTiO_3$	P(VDF-CTFE)	~13	40	~38	7.5	[50]
$SrTiO_3$	PVDF	~10	10	~18	9.1	[51]
$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$	P(VDF-TrFE)	~18	40	~100	–	[55]
NNBT	PVDF	~10	10	~100	–	[56]

a) Dielectric constant of polymer; b) Dielectric constant of filler.

dielectric materials developed in other research studies due to the large aspect ratio of TOMLs, which have a relatively low percolation threshold. Although the dielectric constant of the composite material can be increased by adding conductive and semi-conductive materials, a conductive network is easily formed in the composite material, which will cause unacceptably high dielectric loss and breakdown strength reduction. Typical examples are the dielectric losses of 53 vol-% Ni-P(VDF-TrFE) and 55 vol-% Ni-P (VDF-CTFE), which are around 1 and 0.5, respectively [59].

The interface between the filler and the matrix also has an important influence on the dielectric properties of the composites [62–64]. Generally, the interfacial region of the composite is considered as the physical junction of the different components, and its properties are different from both components. The size of the interface area is varied and greatly related to the nature of the components, the surrounding environment and the strength of the interface. Two classical models, Tanaka's model and Lewis's model, have been proposed to demonstrate the interface. Tanaka's model proposes that the interfacial region between the inorganic nanoparticles and the organic matrix can be divided into three different layers, including a bonding layer, a constraining layer and a loose layer (Fig. 5(a)) [65]. Among them, the interaction strength of the bonding layer with the particles not only affects the thickness of the interface, but also impacts on the dielectric properties of the materials. Lewis's model proposes that the main channel of the leakage current from the inorganic particle filler to the load system is the interface along the nanoparticle [66], as shown in Fig. 5(b). This is due to the equilibrium of the Fermi level or chemical potential, as the functional groups on the surface of filler particles are ionized. Since the surface of the particles is charged, they easily adsorb the charge in the matrix to form a diffusion double layer structure near the interface. Changing the interface structure of the composite materials can alter the electrical conductivity of the composite material.

Due to the large difference in surface energy between the nano-filler and the polymer matrix, the nanoparticles are prone to agglomerating in the polymer matrix during the composite preparation process [67]. Therefore, dispersion of nanoparticles in polymer matrix can render the desired material properties unobtainable. Agglomeration can lead to deterioration of the electrical performance for two reasons: (1) nanoparticle agglomeration facilitates the generation of a leakage path, which increases leakage current and leads to dielectric loss; and, (2) defects and even pores are easily generated by nanoparticles, which cause a reduction in both breakdown field strength as well as in other properties (such as mechanical properties).

The dispensability of the nanoparticles in the organic matrix can be improved by appropriate surface treatments, including surface functionalization with specific groups, polymer encapsulation, and other modification methods [68]. Zhou et al. [69] developed PVDF-based nanocomposites filled with surface hydroxylated $BaTiO_3$ (h-BT) nanoparticles, and showed that surface h-BT has better compatibility with PVDF. Lin et al. [70] improved the compatibility between BT and PVDF by functionalizing the BT surface with dopamine; their experimental results showed that the dielectric constant of the polymer–matrix composite with 50 wt-% dopamine functionalized BT nanoparticles (56.8 at 1 kHz) was 40% higher, compared to pristine BT/PVDF composites (around 40 at 1 kHz). For conductive nanoparticles, the preparation of particles with core-shell structure can block the conductive filler from the matrix and so improve the dielectric properties of the material. Chen and Liu [71] introduced polyaniline/iron core-shell nanoparticles (PANI-CIP) as fillers into PVDF when preparing PANI-CIP dielectric composites (Fig. 6); their results showed that the dielectric constant (72.35 at 0.1 Hz) was 3.5 times larger than that of IP-PVDF.

3.2 Enhancing dielectric strength

Enhancing the breakdown field strength of polymer-based

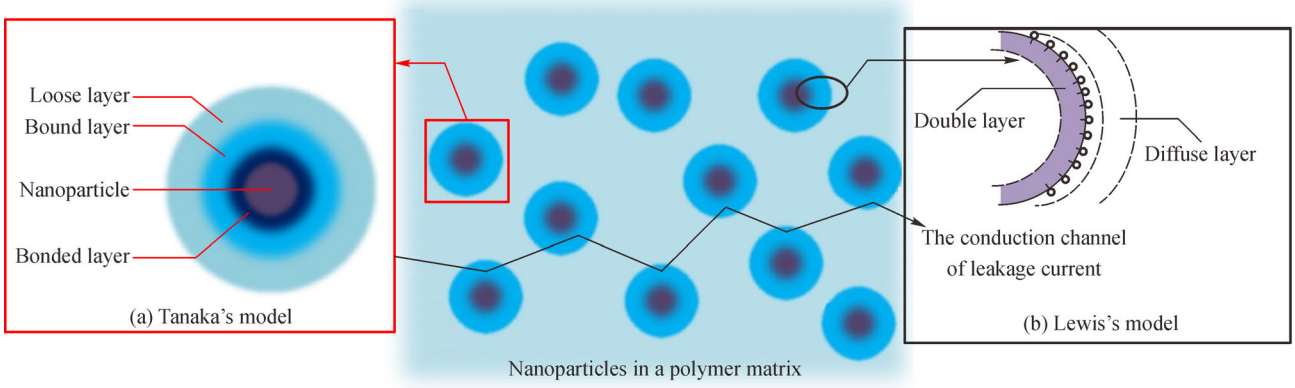


Fig. 5 Schematics of (a) Tanaka's model and (b) Lewis's model.

dielectrics is another beneficial way of increasing the energy storage density. High electrical resistance is also a necessary requirement for high-voltage power systems, such as the HVDC project. Figure 7 shows the power capacitor equipment required in a HVDC transmission system, including capacitors operating on the converter station, a DC filter capacitor and a DC support capacitor. All of these are core equipment to ensure high-quality DC transmission and stable operation of the converter valve [72]. Since these components should be able to withstand high electric voltages of above 100 kV, the breakdown strengths of the energy storage materials are even more important than the energy storage density.

Figure 8 summarizes some of the results reported by researchers in their efforts to improve the breakdown field strength of polymer-based energy storage dielectrics. The methods for enhancing the breakdown field strength of energy storage materials are classified into three groups: fillers without modification, modified fillers, and multi-layered structures.

3.2.1 Blending and hybridization

The breakdown field strength of dielectrics can be effectively increased by blending with other polymers, or hybridizing inorganic fillers to the polymer matrix. A small inclusion of additive would contribute to defects in the crystalline domain and inhibit early polarization saturation at low fields [73]. Zhang et al. [74] introduced thermoplastic polyurethane (TPU) into PVDF in order to prepare TPU/PVDF blend films, which have high breakdown strength (537.8 $MV \cdot m^{-1}$) and high energy density (10.36 $J \cdot cm^{-3}$). Similar results have also been reported for dielectrics into which nanofibers were introduced [75], as those possess a high aspect ratio and thus enhance the breakdown field strength of the polymer matrix. When 1D nanofibers are aligned perpendicular to the applied electric field and oriented in the in-plane direction in the polymer matrix, the tortuosity of the conductive path can be increased with the strong applied electric field, leading to enhancement of the breakdown field strength of the

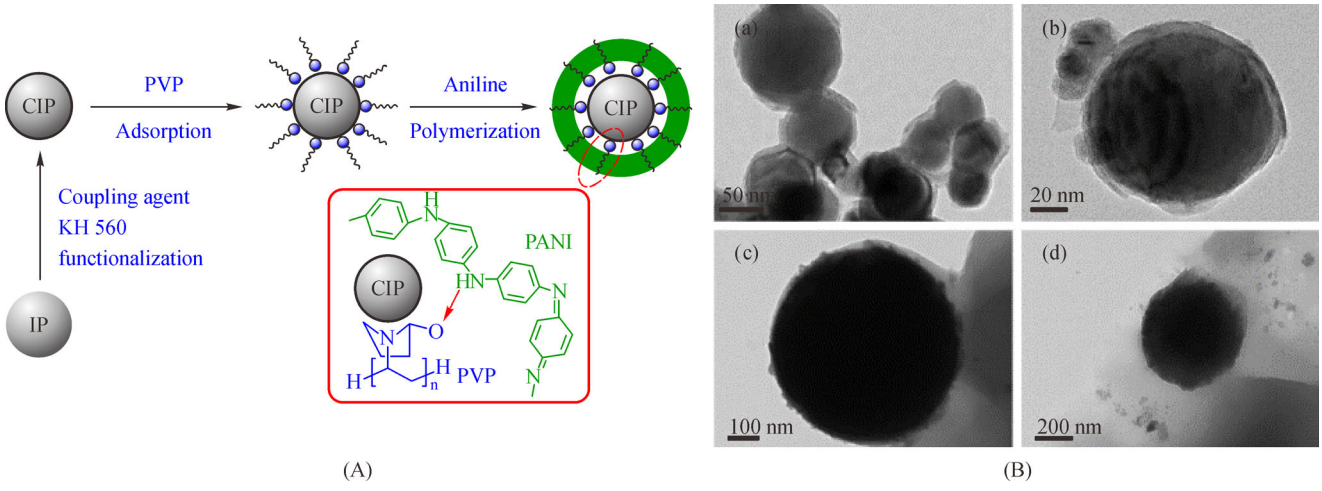


Fig. 6 Schematic representation of the process of synthesizing polyaniline-coated coupling agent functionalized iron powder PANI-CIP core-shell composite (A); TEM images of PANI-CIP (B). Reprinted with permission from Ref. [71]. Copyright 2018, Elsevier.

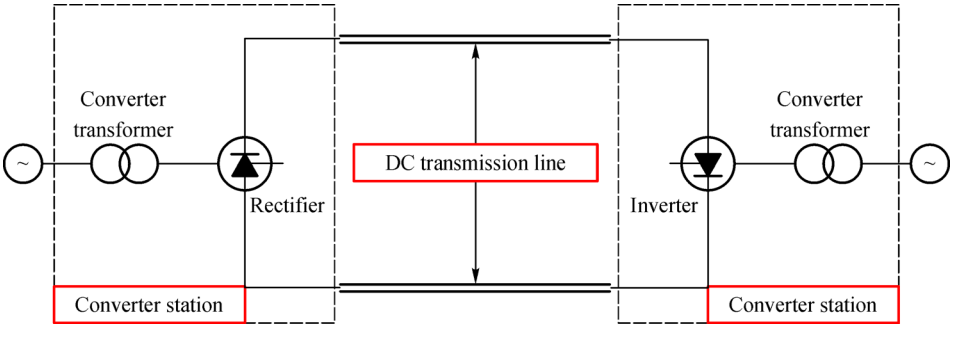


Fig. 7 Schematic diagram of the HVDC transmission project, including AC-DC converter station, DC transmission line and DC-AC converter station.

polymer-based dielectrics [76–80]. This has been verified by Zhang et al., who reported that PVDF with 3 vol-% of BT@TiO_2 nanofibers (about 646 MV·m^{-1}) has higher dielectric strength than pure PVDF (599 MV·m^{-1}) [79]. Alternatively, two-dimensional (2D) nanosheets, such as hexagonal boron nitride nanosheets [81], can be used as conduction barriers to limit charge migration and thus hinder the development of breakdown processes.

When fillers, especially inorganics, are introduced, there arise significant differences in terms of dielectric constant and conductivity between the filler and matrix. They can induce local electric field variation, leading to deterioration in the breakdown field strength of the material, as described in the previous section. It is important to consider smooth variation of dielectric constant and electrical conductivity between the filler particles and the matrix in order to ensure suitable electric field of the materials. Surface functionalization should be employed, and the compatibility and dispersion of inorganic fillers within the polymer matrix should be improved. Xie et al. [82] prepared polydopamine (PDA)-encapsulated BT nanoparticle (PDA@BT)-filled composites using a cross-linked PVDF matrix; their results showed that the PDA coating facilitated homogenous dispersion by forming core-shell structure, which resulted in a 40% improvement in the breakdown strength when compared with crude BT-filled PVDF (Fig. 9). Similar results have also been reported by Luo et al. [83].

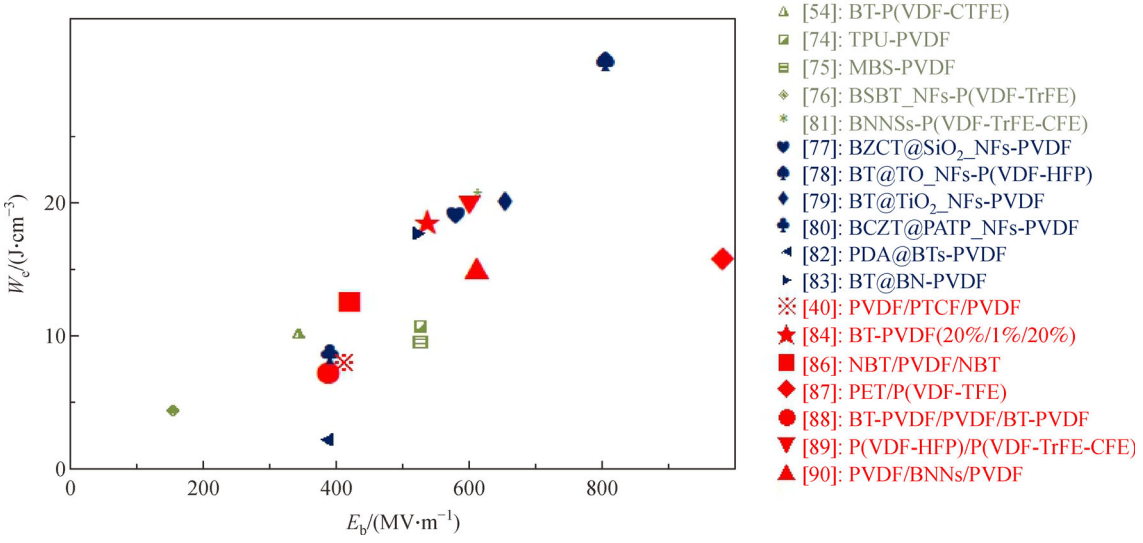


Fig. 8 Breakdown strength and energy storage density of polymer-based dielectrics prepared via different methods. The grey icons indicate methods of improving breakdown field strength by adding filler without modification; the blue icons represent methods involving addition of modified filler; and, red icons indicate methods of constructing multi-layered structures.

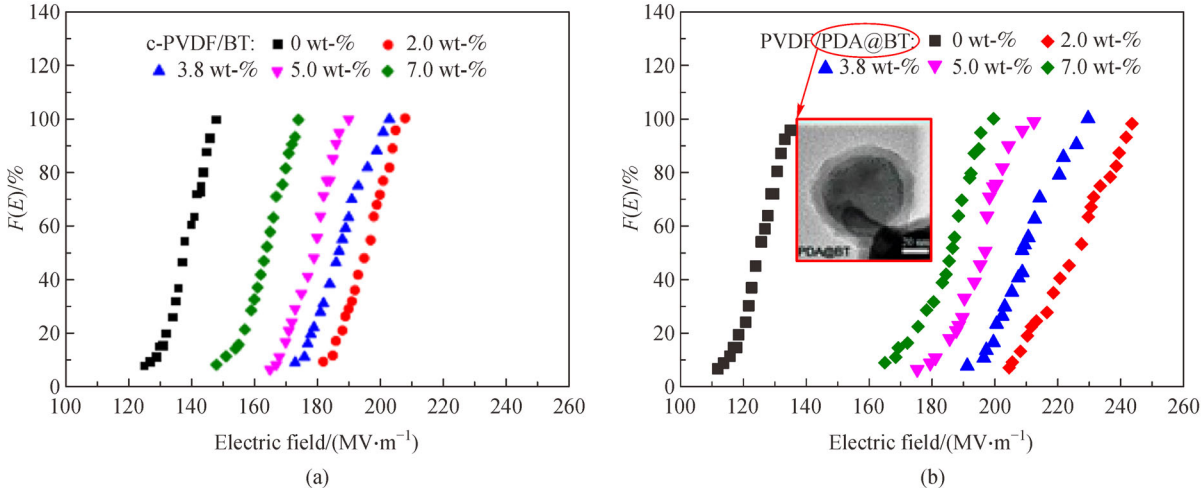


Fig. 9 Weibull distribution of breakdown strength for (a) c-PVDF/BTs, and (b) PVDF/PDA@BTs with different particle compositions at room temperature. Reprinted with permission from Ref. [82]. Copyright 2017, American Chemical Society.

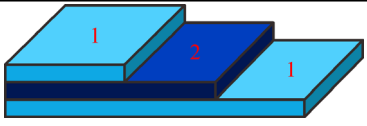
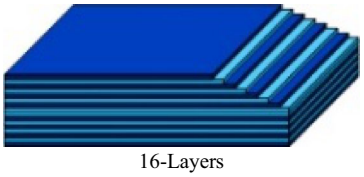
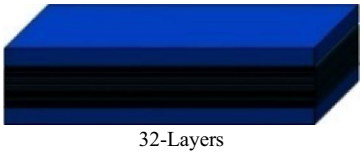
3.2.2 Multi-layer structure design

Structural design, such as preparation of multilayer film, has been demonstrated to effectively improve the breakdown field strength of the polymer [84–90]. Table 3 summarizes some methods for improving the breakdown field strength of energy storage films by changing the macrostructure. Depending on the number of layers used to build the film, this method can be divided into two categories: sandwich structures (including three-layer films), and structures with more than three layers.

A sandwich structure consists of films, with high-dielectric constant layers serving as outer layers, and films with low dielectric constant serving as center layers. The redistribution of the electric field reduces the possibility of breakdown of the intermediate layer, and the strong interface barrier between the outer layer and the central layer hinders the formation of conductive channels. Zhang et al. [40] proposed creating a sandwich polymer structure in order to increase the breakdown field strength of the system; this was performed by combining electrospun P(VDF-TrFE-CFE) fibers with PVDF using a hot-press. The composite material constituting a sandwich structure possesses a strong breakdown field strength (reaching 408 $MV \cdot m^{-1}$), and the energy density under an electric field of 360 $MV \cdot m^{-1}$ is 8.7 $J \cdot cm^{-3}$. Wang et al. [84] proposed a sandwich structure composed of 0–3 composite layers, which has an energy density of 18.8 $J \cdot cm^{-3}$ and a breakdown field strength of 470 $MV \cdot m^{-1}$. If the number of layers exceeds 3, the interface polarization between interfaces is reduced, and the breakdown path becomes more tortuous, which lessens the possibility of breakdown. Carr et al. [87] produced a polymer comprising 32-layer films using poly(ethylene terephthalate) and P(VDF-TFE) copolymer; their results showed that these films had high breakdown fields (about 1000 $MV \cdot m^{-1}$) and high energy density (16 $J \cdot cm^{-3}$).

It can be seen from Table 3 that constructing a multilayer structure can significantly improve the dielectric breakdown field of energy storage materials. However, there is no specific relationship between the dielectric properties of each film and the overall performance, and the role of the optimized number of layers of the films remains unclear. Moreover, the proposed breakdown mechanisms are diverse, and no consensus has been reached. Yin et al. [91] argued that the dielectric breakdown of multilayer films could be described as an electromechanical process, viz. the multilayer film will breakdown when the interfacial charge accumulation overcomes the mechanical strength of charge blocking layer. Pei et al. [92] prepared polymer films with different types of layers, and investigated the mechanisms affecting the breakdown field strength of the two-layer film structure using a serial capacitor model. The high-k (high dielectric constant) layer at the negative electrode suppresses electron injection and improves the breakdown strength of double-layer films. The effect of breakdown strength enhancement is more noticeable when the thickness of the high-k layer is reduced. Although the properties can be enhanced by fabricating multiple-layer structures, such structures are not yet commercially viable as the multilayer film construction requires layers to be well-coupled so as to eliminate defect generation; this is technically complicated and costly.

Table 3 Previous research results on improving breakdown strength through by layer-structure design

Number of layers	Scheme	Materials	E_b/($MV \cdot m^{-1}$)	W_e/($J \cdot cm^{-3}$)	Ref.
Sandwich structure		1:20 vol-% BT-PVDF 2:1 vol-% BT-PVDF	470	18.8	[84]
		1:PVDF 2:PTCF	408	8.7	[40]
		1:1 vol-% NBT-PVDF 2:PVDF	410	12.5	[86]
Multiple layers	 16-Layers	P(VDF-HFP) P(VDF-TrFE-CFE)	637.5	22.6	[89]
	 32-Layers	PET P(VDF-TFE)	~1000	16	[87]

4 Low dielectric loss media for high-power energy transmission

The most significant application of dielectric capacitors is energy storage for high-current transmission across electricity grids. In order to resist the heating effect of power equipment owing to large current, the dielectric loss of the polymer-based dielectrics must be kept very low. Although BOPP has a relatively small dielectric constant (2.2 at 1 kHz), its dielectric loss is extremely low (< 0.0002 at 1 kHz). This gives rise to admirable energy conversion efficiency and low heat generation due to dielectric loss [93], which makes it one of the most extensively used dielectric capacitors in the main energy storage media of electricity grids to date [94].

Compared with BOPP, PVDF and PVDF-based materials have much higher dielectric loss ($\tan\delta > 0.02$) [17], and so the range of applications involving those materials is greatly limited. There are two main types of dielectric loss in ferroelectric polymers: ferroelectric loss, and conduction loss. The former is generated by ferroelectric dipolar switching, which desynchronizes with the applied alternating electric field. The latter is caused by leakage current [81]. Researchers have found that multilayered nanocomposites can suppress conduction losses and so reduce dielectric loss through hindering leakage current. Jiang et al. fabricated P(VDF-HFP)/P(VDF-TrFE-CFE)-multilayered nanocomposites with extremely high charge-discharge efficiency (80%–85%) [89]. Adjusting the polymer-based molecular structure so as to reduce dielectric loss can lower production costs and increase the range of industrial applications. Chen et al. built an asymmetric alicyclic amine-polyethether amine molecular chain structure within a crosslinked epoxy network, and attained low dielectric loss (< 0.006) and very high discharge efficiency (90%) [95].

Another method of reducing ferroelectric losses is by confining crystallization of PVDF so that the ferroelectric loss in the PSF/PVDF system can be reduced [91]. Theoretically, the well-oriented crystals provide a "barrier effect", thus constraining ions' mobility. Further, polystyrene (PS) has a much lower dielectric loss than PVDF when grafted onto P(VDF-CTFE) via free radical polymerization. Following PVDF crystallization, PS forms a constrained layer surrounding the PVDF crystal, leading to lower dielectric loss compared with that following addition of pure PVDF. Optimal properties are achieved at a 34 wt-% PS grafting ratio, with a relatively high discharge energy density (10 $J \cdot cm^{-3}$ at 600 $MV \cdot m^{-1}$) and a low dielectric loss ($\tan\delta = 0.006$ at 1 kHz) [96,97]. Promoting rapid dipole reorientation during discharge by limiting the ferroelectric domains can also reduce the compensating polarization in the polymer [36,98].

5 High working temperature dielectrics

The term 'New energy vehicles' refers to vehicles reliant on an unconventional vehicle fuel as a power source. There have been significant development trends in the automotive industry to develop new energy vehicles in response to growing environmental concerns and fluctuating energy prices [99]. The electric vehicle power inverter module contains a large number of dielectric capacitors, as shown in Fig. 10. Therefore, electric vehicles have strict demands regarding working temperature (operation temperature is about 140°C [100]). This is not a temperature that conventional polymers can withstand.

Although BOPP performs well at a low temperature, it exhibits obvious loss dissipation due to electron conduction when the temperature exceeds 85°C. A large cooling system is required if a BOPP film capacitor is selected for a high-temperature power converter; such an arrangement is impractical. Dielectric polymers with high thermal stability and smaller dielectric loss can help manufacturers bypass this particular problem. The national electrical manufacturers association classifies dielectric polymers into several grades according to their differences in relative insulating index of electrical materials and systems (as shown in Fig. 11).

For amorphous polymers, a high glass transition temperature is generally required. Methods for increasing the glass transition temperature of the polymers include (1) introducing bulky and rigid structures to hinder bond rotation and chain mobility [101]; (2) increasing the polarity of the side groups [102]; (3) generating intermolecular hydrogen bond so as to confine chain mobility; and, (4) crosslinking between molecular chains so as to confine mobility of chain segments. The dielectrics currently used for high working temperature film capacitors can be selected from polymers with high glass transition temperature T_g, such as polyimide (PI), poly (ether imide) (PEI), fluorene polyesters (FPEs), poly(ether ether ketone) (PEEK) [19]. Their physical properties are detailed in Table 4 [103].

Although these polymers are stable at a high temperature, their energy storage densities are relatively low (< 4 $J \cdot cm^{-3}$) at the target temperature. In their efforts to address this, researchers have conducted extensive experiments to improve the energy storage density of these films, such as PI [104–108]. These methods are summarized in Fig. 12, and are similar to those discussed back in Section 3: They include adding high thermal conductive inorganic particles [103] and constructing multilayer film structures [109]. Yin et al. [91] prepared polysulfone-based PSF/PVDF and high-temperature polycarbonate-based HTPC/PVDF multilayer films with 33 alternating layers by means of the forced assembly technique; the resulting film

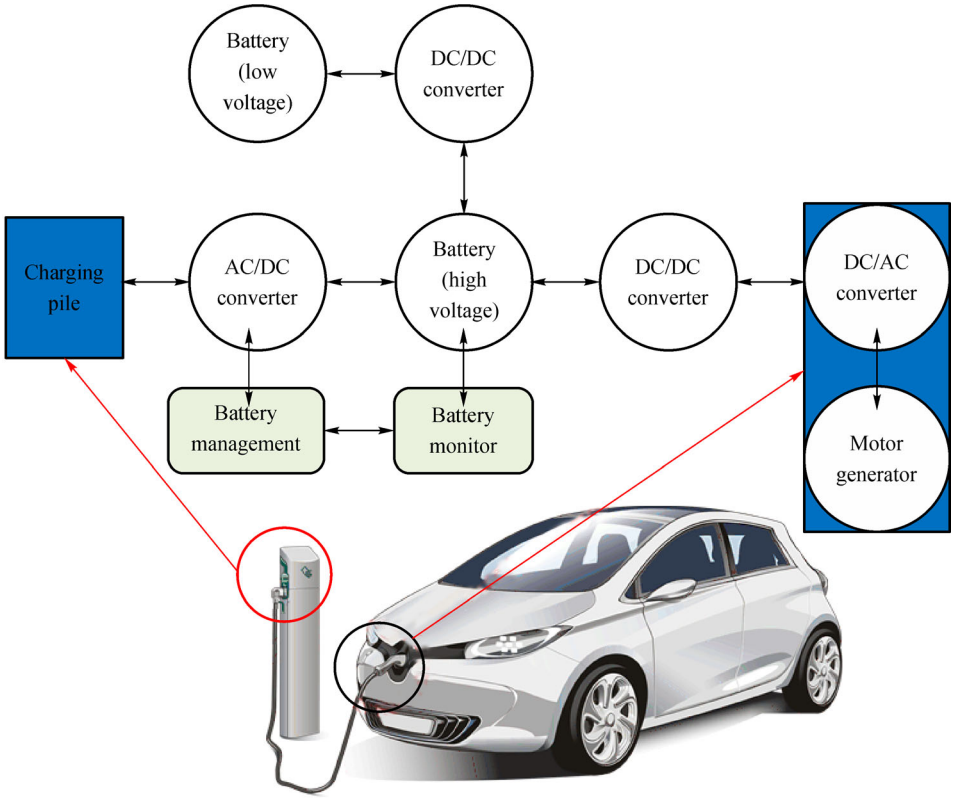


Fig. 10 Schematic diagram of new energy electric vehicles' energy conversion.

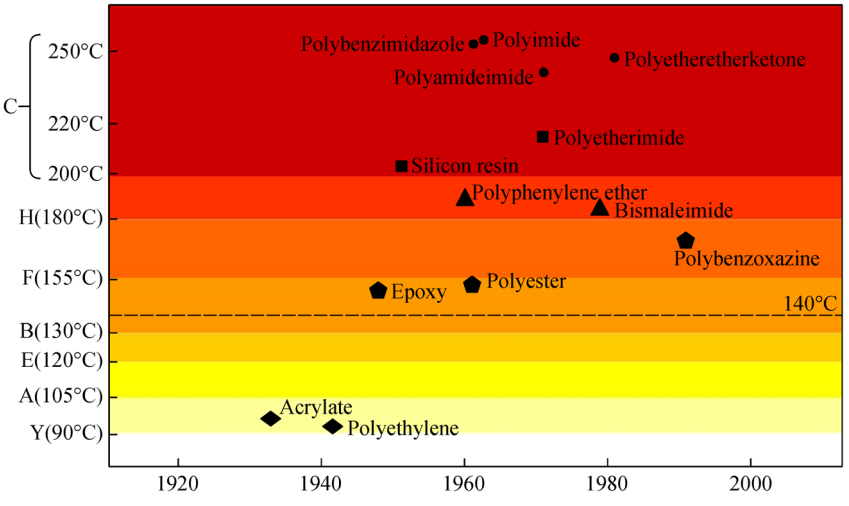


Fig. 11 Common polymer dielectrics and their thermal endurance indices.

thickness was around 12 μm. Since PSF and HTPC exhibit stable dielectric properties even above 150°C, their results demonstrate that both PSF/PVDF and HTPC/PVDF could be potential systems for high temperature capacitor applications.

6 Frequency response for energy storage dielectrics

Response speed is a parameter that is of paramount important in certain specific fields, like pulse power

equipment. The pulse power system releases all stored energy to the load within a very short time interval [110,111]. Figure 13 shows a typical structure of a Marx pulse bank. For most power pulse devices used in particle accelerators, as well as in novel weapons such as inertial restraint devices, laser weapons, and high-power microwaves, the time-scale is required to be within 1 nanosecond or even smaller. Thus, the energy storage media here must be capable of responding extremely quickly, even before high-energy storage density is reached. For generating a pulse with one nanosecond front edge, the energy discharge frequency should be 1 GHz; the main chains and pendent dipole structures of most polymers render this threshold unobtainable [112]. Therefore, special molecular design should be undertaken in order to address this "frequency problem".

Frequency has a strong influence on the dielectric properties of polymeric materials; however, there have been relatively few research studies into the effect of AC-based electric field frequency on energy storage performance [112]. For studies involving polymer-based energy storage materials, the measured frequencies have been set at between 50 Hz and 1000 Hz, a very wide range that allows for a correspondingly wide range of dielectric properties to take place. On the other hand, applications have different requirements in terms of the operating frequency of energy storage materials. For example, P(VDF-CTFE) film experiences a 40% loss in discharged energy density when the discharge time is reduced from 1 ms to 1 μs [113,114]. For capacitors with frequency response, conventional metallization capacitors have high power density but low energy storage density; by contrast, electrochemical capacitors have the characteristics of high-energy storage density but low power density [14]. Neither type of capacitor is appropriate for the above requirements of high-response speed dielectrics. Research activities focusing on this particular problem are quite rare.

Stephanovich et al. [115] found that PVDF and its copolymers permit a slow discharge process, thus releasing less energy in the power pulse system. Guan et al. [98] defined the experimental time t_0 as the time for the discharged energy in the load to reach 90% of the final

Table 4 Physical properties of polymers with high temperature stability

Polymer	ε	tanδ	The highest working temperature/°C	Discharge efficiency
PC	3.2	0.0013	125	~90%
PI	3.1	~0.017	200	94%
PEI	3.2	0.01	200	96%
FPE	3.5	0.0025	200	–
PEEK	3.2	0.004	150	~90%

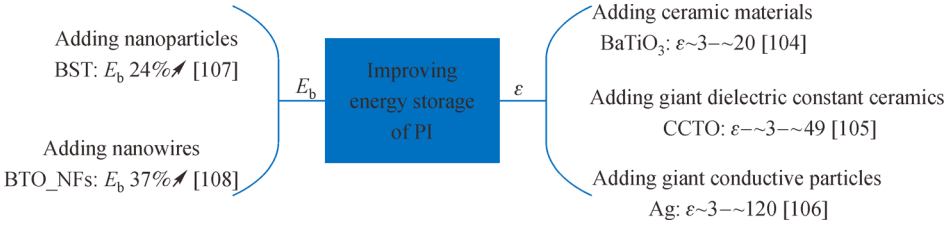


Fig. 12 Methods for improving the energy storage density of PI.

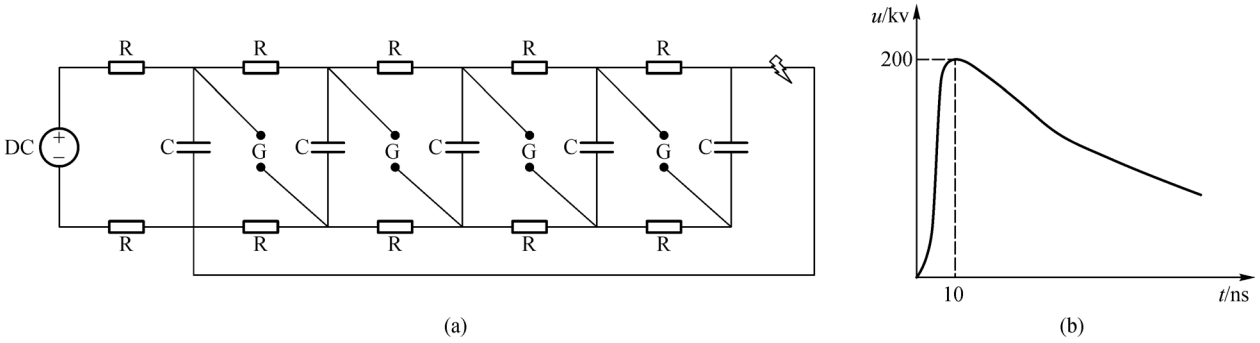


Fig. 13 Schematic diagram of Marx pulse bank and nanosecond pulse waveform.

Table 5 Methods and future application areas of polymer-based energy storage materials (with particular emphasis on different performances and properties)

Performance	Physical parameters	Methods	Application
High energy density	ε E_b	High polar group High permittivity filler Conductive/semi-conductive filler Surface modified filler Multi-layer structure	HVDC project Distributed energy New energy vehicles High power pulse system
Low dielectric loss	tan δ	Multi-layered structure Blending/hybridization.	HVDC project Distributed energy (photovoltaic power/wind power)
High working temperature	Working T	Polymer chain design Inter-chain design (hydrogen bonding/crosslinking)	New energy vehicles
Fast frequency response	Working frequency	Filler design and doping Introduction of high polar atoms and bonds	High power pulse system (inertial restraint, laser weapons, etc.)

value, and they figured out that BOPP and P(VDF-CTFE)-g-PS have a faster discharge compared to PVDF. This is because BOPP consists of linear dielectric materials that do not induce space charge. As for P(VDF-CTFE)-g-PS, there is less space charge induced in the sample due to the confinement effect from the nonpolar PS interfaces surrounding the PVDF crystals. Chu et al. [113] showed that a very high energy density (>17 J·cm^{-3}) with fast discharge speed (<1 μs) and low dielectric loss can be obtained in defect-modified PVEF polymers by combing the reversible nonpolar and polar molecular structures, making it possible to achieve high D with a proper dielectric constant so as to avoid early D-saturation. However, in-depth research into the underlying mechanisms and related structure-property relationships in this field is still lacking.

7 Conclusions and future prospects

This paper reviews published studies on developing polymer dielectric materials for numerous target applications. We emphasize that although high energy density is of paramount important in all applications, other properties, including low dielectric loss, high working temperature and fast frequency response, are of greater importance in certain situations (as summarized in Table 5 below). Until now, much of the research in this field has been concentrated mainly on developing dielectrics with higher energy density for specific applications, while other properties have received less attention. Relatively few studies have considered factors like dielectric loss, and fast frequency response, and consequently there remain barriers which restrict the range of applications for practical devices. This review paper not only has explored methods for enhancing energy density, but has also considered potential avenues for reducing dielectric loss, and achieving high temperature stability and fast-frequency response. We suggest that further development in polymer-based dielectrics should take other application requirements into consideration in order to facilitate industrialization of a wider range of dielectric materials.

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