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High-Temperature Polyimide Dielectric Materials for Energy Storage

*Jun-Wei Zha, Xue-Jie Liu, Yaya Tian, Zhi-Min Dang
and George Chen*

Abstract

The availability of high-temperature dielectrics is key to develop advanced electronics and power systems that operate under extreme environmental conditions. In the past few years, many improvements have been made and many exciting developments have taken place. However, currently available candidate materials and methods still do not meet the applicable standards. Polyimide (PI) was found to be the preferred choice for high-temperature dielectric films development due to its thermal stability, dielectric properties, and flexibility. However, it has disadvantages such as a relatively low dielectric permittivity. This chapter presents an overview of recent progress on PI dielectric materials for high-temperature capacitive energy storage applications. In this way, a new molecular design of the skeleton structure of PI should be performed to balance size and thermal stability and to optimize energy storage property for high-temperature application. The improved performance can be generated via incorporation of inorganic units into polymers to form organic-inorganic hybrid and composite structures.

Keywords: polyimide, thermal property, dielectric property, energy storage, nanocomposites

1. Introduction

With the rapid development of the global economy and a rising population, the search for efficient and clean energy and energy storage technologies has become a priority worldwide. Because of its exceptionally fast energy conversion rate, long life, and environmental friendliness, dielectric energy storage technology has been used in applications for the electronics and power industries such as wearable electronic devices, hybrid vehicles, and weapon systems [1]. As the trend toward high-performance miniaturized electronic devices continues, the demand for dielectric materials with high energy storage density (U_e) is increasing. U_e is an important parameter to measure the energy storage performance of dielectric materials:

$$U_e = 1/2\varepsilon_r\varepsilon_0E_b^2 \quad (1)$$

where ϵ_r is the permittivity of material and ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$) [2]. This requires that the dielectric material has a high ϵ_r while having a low dielectric loss and a high breakdown strength.

Commonly known high-energy storage dielectric materials are mainly biaxially oriented polypropylene (BOPP), polyester, polycarbonate (PC), polyphenylene disulfide, polyurea, polyurethane, and polyvinylidene fluoride [3]. Among many polymers, polyimide (PI) is a type of polymer containing an imide ring on the main chain [4]. PI is widely used in packaging materials, insulation layers, circuit boards, and interlayer dielectrics due to its high tensile strength, excellent mechanical properties, high glass transition temperature (T_g), and good solvent resistance and thermal stability [5]. However, the ϵ_r of polyimide is not sufficiently high (usually less than 10) to meet the requirements of the applications of high-energy density film capacitors.

The chemical groups of a dielectric medium contribute to its molar polarization; as the molar polarization increases, the ϵ_r increases. The dielectric properties (including ϵ_r and dielectric loss) of polymers are mainly related to molecular polarization, which includes electron polarization, vibration polarization (or atomic polarization), orientation polarization (or dipole polarization), ion polarization, and interfacial polarization. However, low-quality/purity polar molecules can reduce the dielectric properties of PI materials [6].

Ma et al. [7] used high-throughput density functional theory (DFT) to rationally design high ϵ_r and band gaps and linked experimental and theoretical results to changes in PI to demonstrate the relationship between chemical functionality and dielectric properties. Currently, researchers usually use two methods to prepare polyimide film capacitors with high ϵ_r , low dielectric loss, and high breakdown strength. One method is directly based on the molecular design of polyimide: Polar groups, conjugated components, or electron-rich groups are introduced into the main polymer chain to increase molecular polarizability, thereby increasing the ϵ_r [8]. The other method, which is currently the most studied, prepares a composite material by introducing high- ϵ_r ferroelectric materials such as TiO_2 , BaTiO_3 (BT), $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, etc. into the polymer matrix to significantly improve the dielectric properties [5].

2. Commercial PI

Kapton PI is an aromatic PI film that has been commercially available since the mid-1960s. Due to its continuous operating temperature of 300–350°C, it is widely used as a high-temperature wire and cable insulation material. At 25°C and 1 kHz, Kapton's ϵ_r is 3.1, but it drops to 2.8 at 300°C. Despite its good thermal stability, Kapton PI cannot be applied to capacitor films because it is difficult to manufacture films with a thickness of $<12 \mu\text{m}$, and problems of carbonization during breakdown. Consequently, research is required to find other PIs with superior dielectric properties. SIXEF-44 is a fluorinated PI (from Hoechst Celanese) prepared from 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) and 2,2-bis(4-aminophenyl)hexafluoropropane (4,4'-6F diamine). This fluorinated PI has a ϵ_r of 2.8 at 1 kHz, T_g of 323°C, and a change in ϵ_r of less than 10% over a temperature range of -55 to 300°C. Other aromatic PIs include: perfluoropolyimide (PFPI; developed by TRW), prepared from the perfluoroisopropylidene diamine of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) and pyromellitic dianhydride (PMDA); and Upilex-S (from ICI), prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine

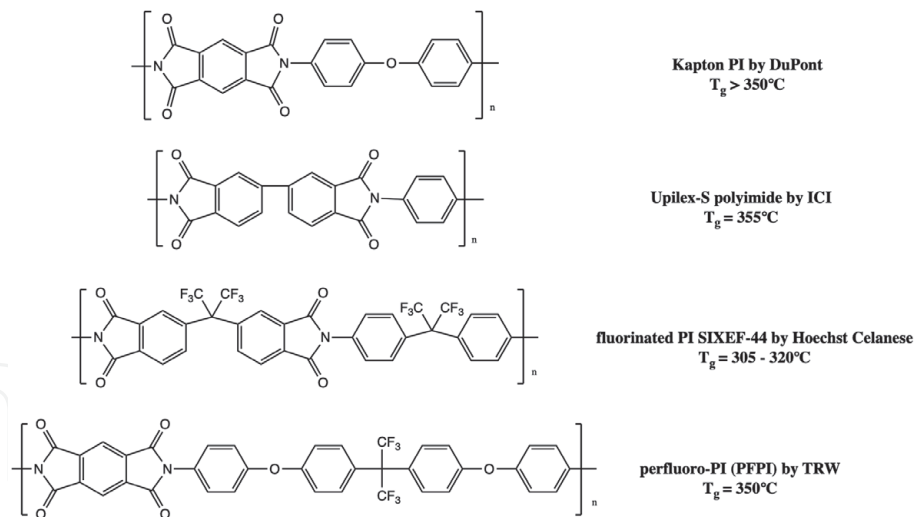


Figure 1.
 Heat-resistant PI polymers used as capacitor dielectrics [9].

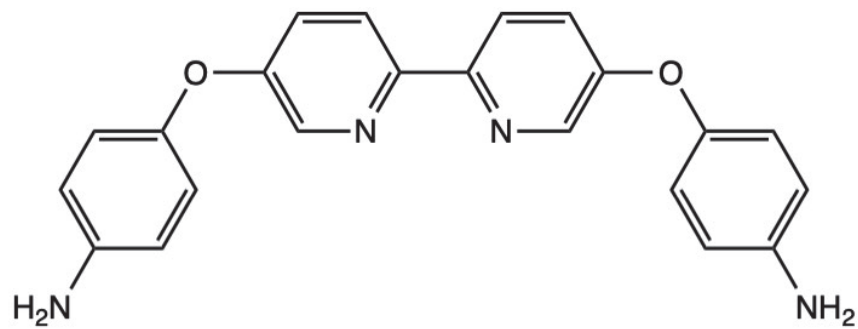
(p-PDA). The T_g of PFPI is $>300^\circ\text{C}$, the ϵ_r is 3.1 at 25°C , and decreases to 2.9 at 300°C ; Upilex-S has a T_g of 355°C , ϵ_r of 3.3 at 25°C and 1 kHz, and remains stable at 300°C . Most of these aromatic PIs affect practical applications due to processing difficulties. A polyetherimide (PEI) called Ultem is modified by the addition of flexible moieties such as ether bonds and alkyl groups in the polymer backbone; it is synthesized from the disodium salt of bisphenol A and 1,3-bis(4-nitrophthalimido)benzene. After development, the PEI film can attain a thickness of $5\ \mu\text{m}$ by melt extrusion and stretching. In order to give PEI flexibility, ether bonds and alkyl groups are added, which results in the following changes (compared to PI): the T_g reduces to circa 215°C ; the ϵ_r increases to 25 at 200°C , and the ϵ_r over 100 Hz–10 kHz is 3.1 [9]. Some of the heat-resistant PI polymers used as capacitor dielectrics are shown in **Figure 1**.

3. Structure modification of PI

The relationship between the dielectric properties of PI and molecular structure can be studied by changing the structure of the aromatic tetracarboxylic dianhydride and diamine monomers used to prepare PI. However, the preparation of the aromatic tetracarboxylic dianhydride is often complex and the yield is low while the synthetic method for phenyl-substituted aromatic diamine is relatively simple, diverse, and high yield. Consequently, modifying the structure of the aromatic diamine monomers has become the primary choice to improve the properties of PIs [10].

3.1 Introduction of bispyridine groups in PI chains

Peng et al. [3] used 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyridine (BPBPA) diamine monomer (as shown in **Figure 2**) and different dianhydrides [BPDA, PMDA, 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-Oxydiphthalic anhydride (OPDA)] to give a series of bispyridyl-containing PIs using a two-step synthesis. The bipyridyl unit enhanced the electronic polarization and coupling: The polarized PI had a ϵ_r of ≤ 7.2 , the dielectric loss was ≥ 0.04 , and the energy density was $\leq 2.77\ \text{J cm}^{-3}$. At the same time, it demonstrated good thermal and mechanical properties.



5,5'-bis[(4-amino)phenoxy]-2,2'-bipyridine (BPBPA,4)

Figure 2.
Dipyridyl-containing diamine monomer [3].

3.2 Introduction of sulfonyl group in PI backbone

Tong et al. [4] studied the relationship between molecular structure and properties using a range of modified PIs. In this study, the ϵ_r was increased by introducing sulfonyl groups, the loss factor was reduced by introducing flexible bonds, and the T_g was increased by retaining the aromatic structure. The resulting sulfonyl-containing PI with different flexible connections gave high ϵ_r (4.50–5.98), low loss coefficients (0.00298–0.00426), high breakdown strength (mostly at 500 MV m^{-1} or more) and high heat resistance (T_g : $244\text{--}304^\circ\text{C}$) (**Figure 3**).

For the anhydride 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA-mDS, each repeat unit contains two $-\text{SO}_2-$, which has the highest dipole density), the ϵ_r was not as high as expected but it can be seen that the two $-\text{SO}_2-$ units improved the stiffness of the overall chain, hindering the rotation of the dipole. Therefore, in addition to the dipole moment and dipole density, the “effective” dipole is another important factor affecting the value of the ϵ_r . Compared to ortho-symmetric OPDA-mDS, para-symmetric PI (OPDA-pDS) was more effective for PI with sulfonyl group (OPDA-pDS) in the diamine moiety (para-para bond). The symmetric structure and low free rotation energy barrier facilitate the alignment of the excimer: The ϵ_r increased to 5.98; the dielectric properties were stable at 150°C ; the discharge energy density and charge and discharge efficiency increased to 7.04 J cm^{-3} and 91.3% at 500 MV m^{-1} respectively [4].

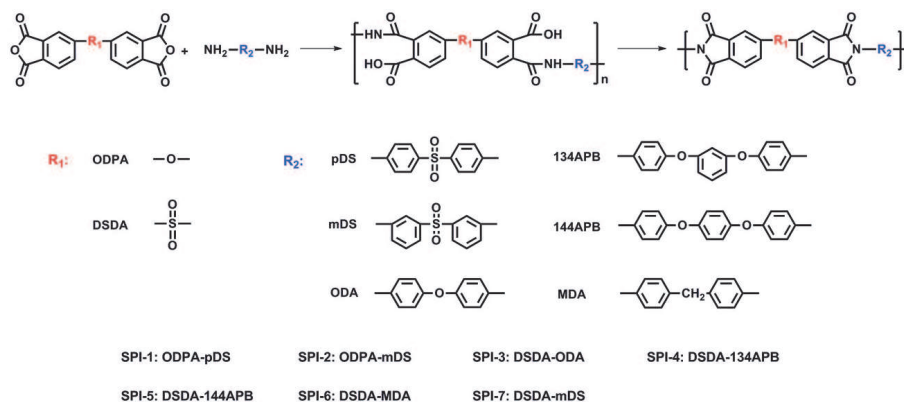


Figure 3.
Synthesis of sulfo-containing PI [4].

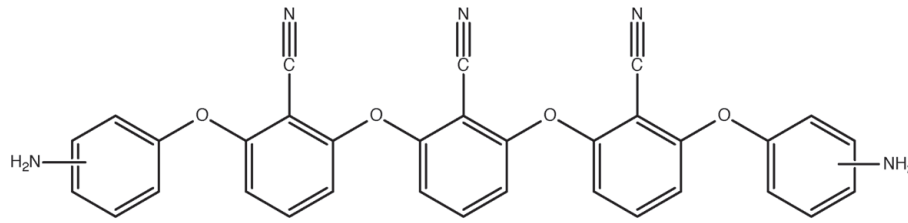


Figure 4.
Diamine monomer containing three nitrile groups [13].

3.3 Introducing nitrile groups in the PI backbone

Due to the high polarity of nitrile groups, special classes of PIs containing nitrile units for piezoelectric and other dielectric applications have previously been studied [11]. Kakimoto et al. [12] reported that attaching a polar -CN side group to a PI could increase its ϵ_r . Treufeld et al. [11] found that adding a CN dipole to the PI main chain had two main effects: Firstly, because the -CN group is directly connected to the main chain in a 90° configuration, the motion is hindered and generates significant friction with randomly stacked adjacent chains, so dipole motion (such as wobble) is introduced into the PI sample; secondly, by adding the -CN group, the PI becomes more polar, easily contaminated by impurity ions, thereby improving ion mobility. Furthermore, it has been shown that the presence of three nitrile groups on the diamine unit is more effective in improving the ϵ_r than one nitrile group. Wang et al. [13] studied and synthesized a series of PIs from a diamine synthesized with three nitrile groups (as shown in **Figure 4**) and four commercial dianhydride starting materials. All PIs showed a high T_g , thermal stability and excellent mechanical properties; the PI had a ϵ_r of 4.7 resulting from the introduction of three highly polar nitrile groups.

3.4 PI grafted with phthalocyanine oligomer at amino terminal

Unlike ordinary composite materials, graft polymers, with good properties, were synthesized by Chen et al. [7]. The copper phthalocyanine oligomer (o-CuPc,

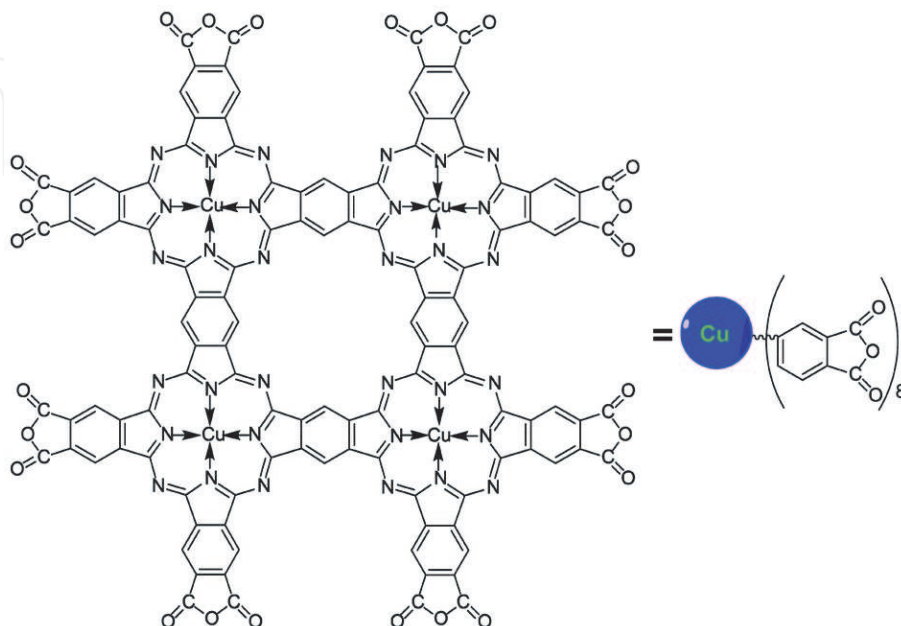


Figure 5.
Synthetic copper phthalocyanine oligomer [7].

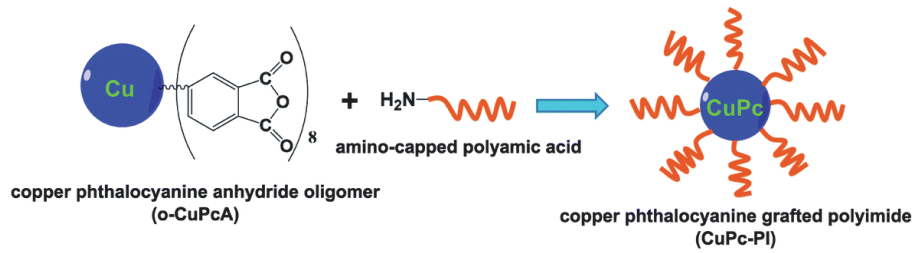


Figure 6.
Schematic diagram of graft reaction [7].

shown in **Figure 5**) is a semiconductor material with unique electrical properties ($\epsilon_r > 103$) and good thermal stability, used widely in organic optoelectronics, the dye industry, catalysis, electrochromism, and electroluminescence display and other fields. The design and synthesis resulted in a high- ϵ_r all-organic polymer material, that is, a CuPc-PI homogeneous block copolymer was prepared (see **Figure 6**). The CuPc-PI also showed low dielectric loss, high breakdown strength, high U_e , high thermal stability, and good mechanical properties; its overall performance was higher than the direct use of o-CuPc/PI composites obtained using CuPc as the conductive filler [7].

4. Polyimide-based composite dielectric materials

4.1 Simple compound

Modification of the molecular structure of the polymer can improve its dielectric properties although the effect can be small. Using a simple compounding method with a high ϵ_r filler (e.g., ceramic filler, conductive filler), a polymer with a high breakdown field strength can be obtained. This procedure has gained acceptance due to its simple preparation method.

The conductive filler polymer-based composite material can attain a high ϵ_r for relatively small additions of filler, and the large increase in ϵ_r can be explained by the percolation theory. Adding filler at the percolation threshold will greatly increase the electrical conductivity and ϵ_r of the composite material, thereby improving the transition layer between the filler and the matrix. Carbon materials such as carbon nanofibers (CNFs), carbon black, carbon nanotubes (CNTs), graphene, and graphite flakes are most commonly used in recent research. Among these conductive fillers, CNTs are a good choice due to their high electrical and thermal conductivity and high aspect ratios. Wu et al. [14] functionalized multi-walled carbon nanotubes (MWCNTs) with carboxyl groups prior to dispersing into PI nanofibers using electrospinning technology. Hot pressing was then performed to produce high-performance PI/MWCNT composites with a high ϵ_r , good mechanical flexibility, and excellent thermal stability. When the concentration of MWCNT was close to the percolation threshold of 12–14 vol%, the material showed a high ϵ_r , low breakdown strength, and maximum U_e . When the MWCNT content was 12 vol%, the maximum U_e was 1.957 J cm^{-3} , which was 4.8 times that of pure PI (0.404 J cm^{-3}), and the dielectric loss was less than 0.1. As a two-dimensional nanomaterial, graphene has great potential in the future because it can improve the mechanical, thermal, and electrical properties of polymers. Among these materials, graphene oxide (GO) has also been reported in some articles to improve the mechanical properties and thermal stability of polymer-based composites. Chen et al. [15] prepared pure PI, PI/GO, and PI/reduced GO (rGO) films by in situ

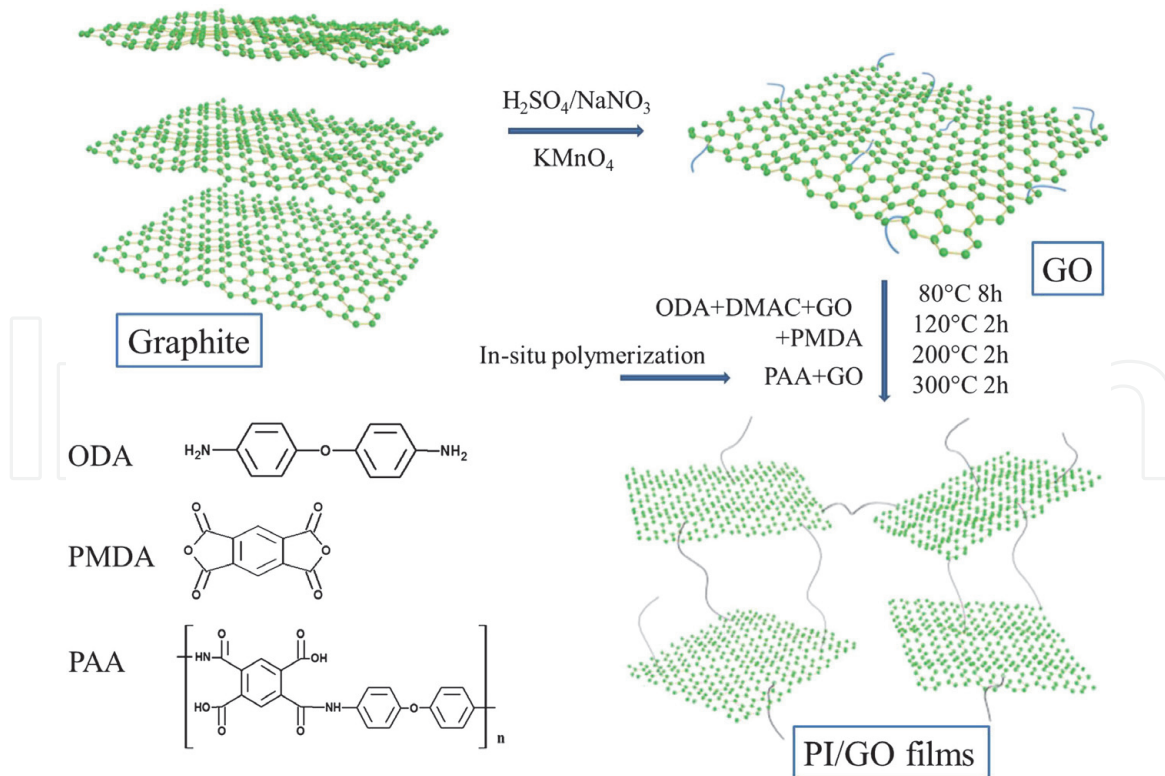


Figure 7. Schematic illustration of the film preparation procedure for GO and PI/GO composites [15].

polymerization, as shown in **Figure 7**. Among them, PI/GO and PI/rGO films both demonstrated improved thermal stability compared to pure PI films. Furthermore, at 100 Hz, when the mass fractions of GO and rGO were 2 wt%, ϵ_r were also improved (4.9 and 5.8, respectively).

Adding conductive particles as a filler to the polymer matrix can improve the ϵ_r of the polymer composite. When the added amount is close to the percolation threshold, the ϵ_r can be significantly increased. However, as the amount of addition increases, a conductive network is formed, and their dielectric loss will increase sharply. In general, nanostructured BT fillers and BT-based nanocrystals are the more promising materials due to their excellent dielectric and ferroelectric properties [16].

Fan et al. [17] studied the relationship between the ϵ_r and the temperature for thermosetting PI matrix nanocomposite films containing BT nanoparticles at 10^3 Hz. Two temperature changes were reported, namely heating from 50 to 150°C and cooling from 150 to 50°C to investigate the effects of the transition of the BT crystal phase and the free volume change in PI on the ϵ_r for BT/PI nanocomposite membranes. Theoretical models were also used to predict the ϵ_r of composite materials to study the role of the diameter and shape of the nanoparticles. Rajib et al. [18] prepared BT/PI nanocomposites and increased their energy density at high temperatures using different volume fractions to analyze their effect on the dielectric properties. All samples were tested at high temperatures to evaluate their energy storage capacity. The highest U_e was found when the volume fraction of BT was 20% reaching 9.63 J cm^{-3} at 20°C and 6.79 J cm^{-3} at 120°C. As a dielectric material, it is expected to maintain a high energy density value at a temperature of 120°C. A pure PI film prepared by Sun et al. [19] showed high breakdown strength (451 kV mm^{-1}) and high energy density (5.2 J cm^{-3}). The introduction of BT nanoparticles increased the ϵ_r of the nanocomposite to 6.8, while the dielectric loss was still relatively low (0.012 at 10^4 Hz). However, a small amount of (3 vol%) BT nanoparticles also caused a significant decrease in the breakdown field strength (275 kV mm^{-1}), which greatly reduced the energy density (1.7 J cm^{-3}) of the BT/PI nanocomposite.

Therefore, for BT/PI nanocomposites, future research may concern improvements in the thermal conductivity of nanocomposites and the formation of interpenetrating networks throughout the polymer matrix. Improvements in this area will make nanocomposites less susceptible to breakdown [19]. Wang et al. [20] successfully prepared BT nanowire/PI (BT-NW/PI) and BT nanoparticle/PI (BT-NP/PI) composites with low volume fractions. Due to strong interfacial polarization, the ϵ_r of BT-NW filled composites was greater than that of BT-NP/PI. The ϵ_r of the composite containing 5 vol% BT-NW was 6.6 at 100 Hz, which was 94% higher than pure PI ($\epsilon_r = 3.4$ at 100 Hz) and 22% higher than that of composite containing 10 vol% BT-NP ($\epsilon_r = 5.4$ at 100 Hz). In addition, BT-NW also significantly improved the U_e of the composite. When the content of BT-NW was 2 vol%, the U_e obtained at 2200 kV cm^{-1} was 1.06 J cm^{-3} , which was 37% greater than pure PI. Therefore, it could be shown that the introduced linear ceramic filler had a positive effect on the dielectric properties and U_e of the composite material [20]. Hu et al. [1] prepared and studied the dielectric properties of a BT nanofiber/PI (BT-NF/PI) composite membrane over the temperature range $20\text{--}200^\circ\text{C}$. The introduction of BT-NF at 9 vol% increased the ϵ_r for BT-NF/PI to 8.3 while the dielectric loss increased only slightly; these effects could be attributed to dipolar polarization and interfacial displacement of the nanocomposites. The breakdown strength of BT/PI composites containing 1 vol% BT-NF reached 550 kV mm^{-1} , and the discharge energy density reached 5.82 J cm^{-3} . Additionally, the introduction of BT-NF reduced the leakage current and improved the heat conduction. At 1 vol% BT-NF, the PI nanocomposites also exhibited high energy utilization efficiency and good thermal stability. At 150 and 100°C , when the efficiency was greater than 90%, the discharge energy density values were $>2.1 \text{ J cm}^{-3}$ and $\approx 4 \text{ J cm}^{-3}$, respectively [1]. The authors used electrospinning to prepare BT-NF while the PI composite membranes were prepared by in situ dispersion polymerization. The dielectric properties of BT-NF/PI composite films in the frequency range of $10^2\text{--}10^6 \text{ Hz}$ at a temperature of $20\text{--}150^\circ\text{C}$ were studied. The results showed that the ϵ_r of the PI nanocomposite film with 30 vol% BT-NF at 100 Hz increased to ≈ 27 while the dielectric loss was only 0.015.

Furthermore, the calcination temperature of BT has a significant influence on the ϵ_r of the PI/BT-nanocomposite film as shown in **Figure 8**. The ϵ_r of the PI composite film calcined at 1000°C was higher than the PI composite films calcined at 600 and 800°C ; when the BT-NF content was 30 vol%, the ϵ_r of the BT-NF/PI composite film increased to 26.6 [16]. Beier et al. [21] added $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST)

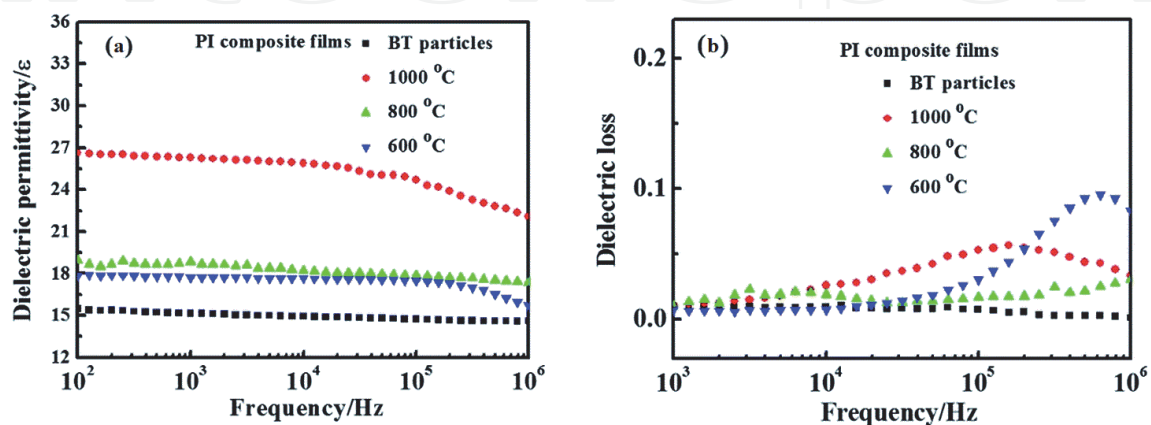


Figure 8. Frequency dependence of dielectric property of 30 vol% BT nanoparticles (a) dielectric permittivity and (b) dielectric loss measured at room temperature [16].

nanocrystals to the PMDA-1,3-bis(4-aminophenoxy)benzene (BAPB) PI system to generate nanocomposites. Compared with the ϵ_r (2.8) of pure PMDA-BAPB PI, the ϵ_r of composites containing 18 vol% BST increased to 6.2; below 1 MHz, the dielectric loss of composite materials with different contents of BST was less than 0.04. At an addition level of 10 vol% BST, the breakdown strength of PMDA-BAPB/BST nanocomposites increased, to reach a maximum value $296 \text{ V } \mu\text{m}^{-1}$, while the energy density of the composite was twice that of pure PMDA-BAPB PI. The observed relative increases in ϵ_r and breakdown strength together with the reduction in dielectric loss for the nanocomposite with 10 vol% BST are desirable characteristics for practical applications [21]. Wang et al. [22] prepared PI-based composites with good dielectric properties using $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) and Zr-modified $\text{CaCu}_3\text{Ti}_{3.95}\text{Zr}_{0.05}\text{O}_{12}$ (CCTZO) particles as fillers. The results showed that at a filling content of 40 vol%, the ϵ_r of the CCTZO/PI composite film could reach a value of 70 at 10 Hz, and this was higher than that of the CCTO/PI composite film under the same conditions; at 150°C , the ϵ_r of the CCTZO/PI composite material reached ≈ 260 [22].

By changing the design of the inorganic filler, interface problems between the filler and the polymer can be improved, such as poor flake/fiber morphology. The nanosheets can increase the breakdown strength of composites because they provide a uniform insulating center and a curved path for the electrons. Boron nitride nanosheets (BNNSs) have a layered structure like graphene and are wide band gap (6 eV) insulators. Unlike traditional dielectric materials (high- ϵ_r ceramics and conductive fillers), polymer/BNNS nanocomposites may provide higher breakdown field strengths. Wan et al. [23] prepared three-phase composites of BNN, BT-fibers, and PI (BNNS@BT-fiber/PI) using in situ polymerization. The combination of BNNS and BT fibers can facilitate the dispersion of BNNS nanosheets in BT fibers, thereby improving energy storage performance. When the content of BNNS@BT-fiber was 20% by weight, the ϵ_r of the composite material was 47.57 at room temperature and 43.03 at 200°C at 100 kHz, demonstrating a reasonable thermal stability. At a BNNS@BT-fiber content of 1 wt%, the maximum U_e of the composite at 3438 kV cm^{-1} was 7.1 J cm^{-3} , that is, about three times that of pure PI [23].

In order to achieve better dispersion and alignment of the filler in the PI matrix, Gu et al. [24] prepared micron boron nitride (mBN)/PI composites by in situ polymerization and electrostatic spinning technology. At 30 wt% mBN, the mBN/PI composite material exhibited a high ϵ_r (3.77) and low dielectric loss (0.007); the material also showed good thermal stability ($\lambda = 0.696 \text{ W m}^{-1} \text{ K}^{-1}$), a high temperature index (279°C), and T_g was 240°C [24]. Cheng et al. [25] considered that molybdenum disulfide (MoS_2) had an appreciable band gap and excellent heat resistance, and prepared MoS_2 /PI nanocomposite films. Compared with the pure PI film, the ϵ_r of the composite film was significantly increased, while the dielectric loss remained relatively low. At a filler content of 1 vol%, the breakdown field strength reached 395 MV m^{-1} , while U_e increased to $\approx 3.35 \text{ J cm}^{-3}$. Furthermore, at 395 MV m^{-1} , the charge and discharge efficiency could still be maintained above 80% [25]. Alumina (Al_2O_3) filler has good insulation performance, high thermal conductivity, and is relatively inexpensive. Therefore, it can be added to the polymer matrix as a filler to improve thermal performance. Choi et al. [26] used 6FDA, 4,4'-methylenedianiline, and bis(3-aminopropyl)-terminated polydimethylsiloxane to prepare PI films with different siloxane content. Since PI-3, PI-4 and PI-5 films were independent and flexible, PI/ Al_2O_3 composite films were prepared at different concentrations of Al_2O_3 using these three PIs. The results showed that the thermal conductivity of the composite film increased with increasing Al_2O_3 content. The composite film containing 75% by weight of Al_2O_3 was flexible. The composite film containing 80 wt% Al_2O_3 showed improved thermal conductivity ($>1.3 \text{ W m}^{-1} \text{ K}^{-1}$).

Compared with traditional polysiloxane/ Al_2O_3 composite materials, PI/ Al_2O_3 composite films demonstrated improved thermal properties [26].

4.2 Surface modification

Because of its simple method, the compounding of fillers and polymers to produce composite materials has become accepted. However, preparation methods, external conditions, and other complications can give rise to many structural defects and electric field concentrations between the two phases of the filler and the polymer matrix. Therefore, surface treatment of the filler using a coupling agent, or decorative insulating, or conductive particles has become a key area of research [27, 28].

Halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) is an aluminosilicate clay, which has a unique tubular structure. It has a high ϵ_r (6–8), but extremely low dielectric loss (10^{-3}). Because there are moderate hydroxyl groups on the surface that can be chemically modified, and suitable surface modification can be performed, halloysite nanotubes (HNTs) may be an ideal filler for the preparation of dielectric polymer-based composites with high ϵ_r and low dielectric loss characteristics. Zhu et al. [29] used KH550 (3-aminopropyltriethoxysilane) and polyaniline (PANI) to modify the surface of HNT, and prepared HNT/PI, KH550 modified HNT/PI and PANI-HNT/PI nanocomposite membranes. Among these, at 100 Hz, the PANI-HNT/PI films attained a maximum ϵ_r of 17.3, while the dielectric loss was only 0.2. Notably, the prepared composite has high breakdown strength ($>110.4 \text{ kV mm}^{-1}$), and a maximum discharge energy density of 0.93 J cm^{-3} ; these properties could still be maintained at temperatures $\leq 300^\circ\text{C}$ [29]. Wang et al. [30] prepared a nanocomposite with high thermal conductivity by introducing amide-functionalized MWCNT [MWCNT@p-phenylenediamine (PPD)] into a PEI matrix, as shown in **Figure 9**. Compared with unmodified MWCNT, MWCNT@PPD could participate in the in situ polymerization of PEI to form covalent bonds in the matrix, thereby improving the dispersibility of the filler. This method solved the disadvantages of the traditional CNT acid treatment that can destroy their conjugate structure and greatly affect the aspect ratio. The results showed that the thermal conductivity of nanocomposites containing 4.0 wt% MWCNT@PPD $\leq 0.43 \text{ W m}^{-1} \text{ K}^{-1}$ [30].

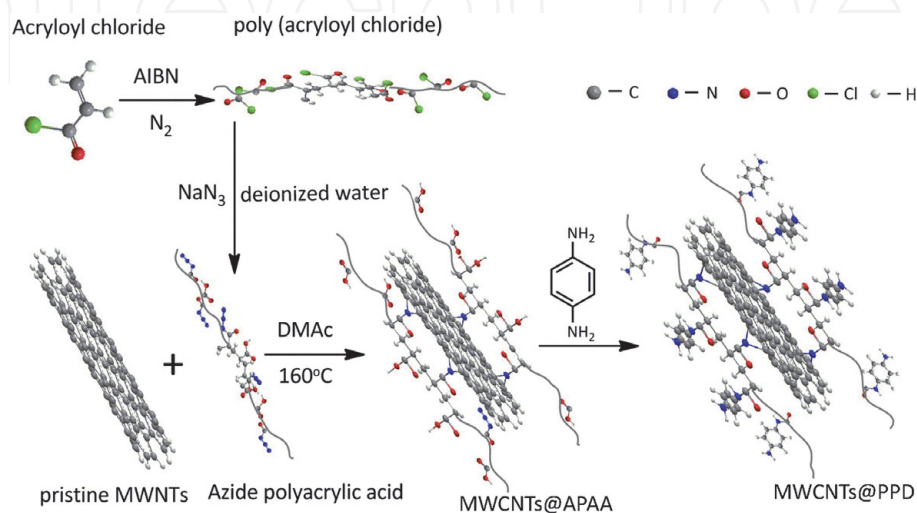


Figure 9. Schematic for the preparation of multi-walled carbon nanotubes@azide polyacrylic acid (MWCNT@PPD) [30].

Yang et al. [27] investigated the dielectric properties of PI incorporating CCTO/Ag nanoparticles (CCTO@Ag). The use of Ag coating to modify the surface of CCTO nanoparticles increased the conductivity of the intermediate layer, thereby enhancing the space charge polarization and Maxwell-Wagner-Sillars effect, improving the electric field distortion. The results showed that when the content of CCTO@Ag was 3 vol%, the ϵ_r of PI/CCTO@Ag composites was significantly increased to 103, which was about 30 times the ϵ_r of pure PI. At the same time, the dielectric loss was very low at 0.018 [27]. Wang et al. [31] used 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) and TH-615 acrylic-acrylate-amide copolymers to modify BT nanoparticles, and then prepared a BT/PI composite film by in situ polymerization. The results showed that this surface modification method could improve the dispersion uniformity of filler particles in the matrix and improve the interfacial compatibility between the two phases. At 10^3 Hz, a BT/PI film modified with 8% PBTCA had a ϵ_r of 23.5, a dielectric loss of 0.00942, a breakdown strength of 80 MV m^{-1} , and a U_e of 0.67 J cm^{-3} . At the same frequency, the composite modified with 6% TH-615 had a ϵ_r of 20.3, a dielectric loss of 0.00571, a breakdown strength of 73 MV m^{-1} , and a U_e of 0.68 J cm^{-3} [31]. Due to its unique chemical structure, GO shows great potential in the field of capacitors. The graphene oxide sheet has many hydroxyl groups and epoxy groups on the surface while carboxyl groups are mainly located on the edges. However, most studies involving graphene-based composites have used only marginal carboxyl groups, so the polymer chains were attached to the edges only. Fang et al. [32] made full use of oxygen functional groups to prepare PPD-carboxyl-functionalized graphene oxide (CFGO)/PI composites. The polymer chain was fixed on the base surface, and the graphene oxide sheet was effectively separated. Thermogravimetric analysis (TGA) tests showed that PPD-CFGO/PI composites had good thermal stability below 500°C . When the content of PPD-CFGO was 4 wt%, the ϵ_r increased to 36.9, which was 12.5 times higher than that of pure PI polymer (≈ 3.0), the dielectric loss was only 0.0075, and the breakdown strength remained at a high level [32].

However, the covalent functionalization method adopted by Fang et al. [32] reduced the conductivity of graphene by destroying the π - π conjugate structure of graphene. In order to overcome this shortcoming, Feng et al. decorated the surface of rGO with a solid π - π stack by insulating reduced polyaniline (R-PANI) to introduce a space effect and effectively prevent the irreversible agglomeration of rGO. At 1 kHz, the highest ϵ_r (25.84) was observed in nanocomposite films containing 20 wt% rGO@R-PANI, and the dielectric loss was 0.11. The ϵ_r and dielectric loss of rGO/PI nanocomposite films were 8.23 and 56.4, respectively. Furthermore, the 5 wt% weight loss temperature for 20 wt% rGO@R-PANI/PI nanocomposite film was 480°C , indicating that the nanocomposite film has great potential in the field of high-temperature dielectric materials [5]. Yue et al. [5] introduced reduced barium titanate (rBT), sintered in a reducing atmosphere ($95\text{N}_2/5\text{H}_2$), to PI without using any modifier or surfactant ingredients in the matrix. Surface defects of rBT and interface interactions between two phases caused by the reducing atmosphere lead to an increase in ϵ_r and U_e . Compared with pure PI, the rBT/PI composite with 30 wt% rBT exhibited the following characteristics: The ϵ_r at 1000 kHz was ≤ 31.6 (pure PI = 4.1), the material maintained a low dielectric loss (0.031), the U_e of 9.7 J cm^{-3} at 2628 kV cm^{-1} represented an increase of $>400\%$ (for pure PI $U_e = 1.9 \text{ J cm}^{-3}$ at 3251 kV cm^{-1}) [5].

4.3 Core-shell structure

Recently, much work has focused on introducing an intermediate layer or an insulating shell on the surface of the filler to prevent them from directly connecting

to each other. Fillers in composite materials can increase electrical conductivity and cause excessive polarization interfaces. Researchers are also attempting to introduce intermediate layers or oxide shells between fillers to reduce dielectric loss. Studies have also shown that the core-shell structure can achieve a high ϵ_r , low dielectric loss, and high energy density [28, 33].

Liu et al. [34] synthesized a sandwich-shaped core-shell $\text{SiO}_2@\text{GO}$ hybrid to prepare a novel $\text{SiO}_2@\text{GO}/\text{PI}$ flexible composite film using in situ polymerization. The dense SiO_2 layer grafted onto the GO surface can effectively suppress leakage current. The results showed that at 40 Hz, the ϵ_r of the composite material containing 20 wt% $\text{SiO}_2@\text{GO}$ was as high as 73, which was 21 times that of pure PI (3.0), and the dielectric loss was only 0.39. In order to improve interfacial compatibility, two coupling agents, 3-aminopropyl triethoxysilane and 3-glycidoxypropyltrimethoxysilane (GPTS), were used to modify the surface of $\text{SiO}_2@\text{GO}$: At 40 Hz, the ϵ_r of the GPTS- $\text{SiO}_2@\text{GO}/\text{PI}$ composite increased to 79 and the loss decreased to 0.25. This significant improvement in the dielectric properties was due to the improved dispersibility of the filler following GPTS modification. Wang et al. [28] prepared a core-shell structure of $\text{BT}@\text{SiO}_2$ nanofibers by electrospinning, and successfully prepared a nanocomposite membrane composed of core-shell $\text{BT}@\text{SiO}_2$ nanofibers and PI. Because SiO_2 has very low dielectric loss (0.00002) and moderate ϵ_r , using a thin layer of SiO_2 to isolate PI from BT nanofibers can alleviate the local field concentration. The latter is caused by the large difference in ϵ_r between the concentrations of the two phases, thereby enhancing the breakdown strength of the PI nanocomposite film. Compared with pure PI, the composite film filled with 3 vol% $\text{BT}@\text{SiO}_2$ nanofibers had a maximum U_e of 2.31 J cm^{-3} at 346 kV mm^{-1} (pure PI $U_e = 1.42 \text{ J cm}^{-3}$ at 308 kV mm^{-1}). TGA also showed that below 500°C , $\text{BT}@\text{SiO}_2/\text{PI}$ nanocomposite films had good thermal stability [28]. Wang et al. [35] prepared a core-shell AgNW/PI composite film with high ϵ_r and low loss (see **Figure 10**). The insulating shell could protect the silver cores from being directly connected to each other, so that when the ϵ_r of the composite film reached its maximum value (126), the dielectric loss remained at a low level [35].

Weng et al. [33] synthesized a novel core-shell of $\text{Ag}@\text{Al}_2\text{O}_3$ nanoparticles as conductive fillers and doped them into PI to prepare $\text{Ag}@\text{Al}_2\text{O}_3/\text{PI}$ composite films. The composite film containing 10% by weight of $\text{Ag}@\text{Al}_2\text{O}_3$ had a ϵ_r of 21, which was seven times higher than that of pure PI (3.1). This increase in ϵ_r may be due to the high electrical conductivity of the $\text{Ag}@\text{Al}_2\text{O}_3$ filler, which caused interfacial polarization inside the composite in the applied electric field. Hence, when the mass fraction of $\text{Ag}@\text{Al}_2\text{O}_3$ was increased to 30%, the maximum value of ϵ_r was 124 [33].

4.4 Multilayer structure

Most polymer nanocomposites are expected to achieve high energy density by combining the high breakdown strength of the polymer matrix with the high ϵ_r of the filler. In fact, when the filler is introduced into the polymer matrix, the breakdown strength often decreases, especially when the volume fraction of the composite filler is high, which does not improve the energy density of the nanocomposite. Therefore, there is a need to expand nanocomposites into multilayer structures to compensate for the reduced breakdown strength [36].

Chen et al. [36] designed a three-layer PI composite membrane by combining $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (KTN) nanoparticles with PI. Pure PI (with high breakdown field strength) was used as the middle layer with KTN/PI nanocomposite as the two outer layers to improve the energy storage performance of the entire composite film. The results showed that the maximum discharge energy density of the triple-layer composite film (t-KPI) was 3.0 J cm^{-3} at 300 kV mm^{-1} , which was much larger

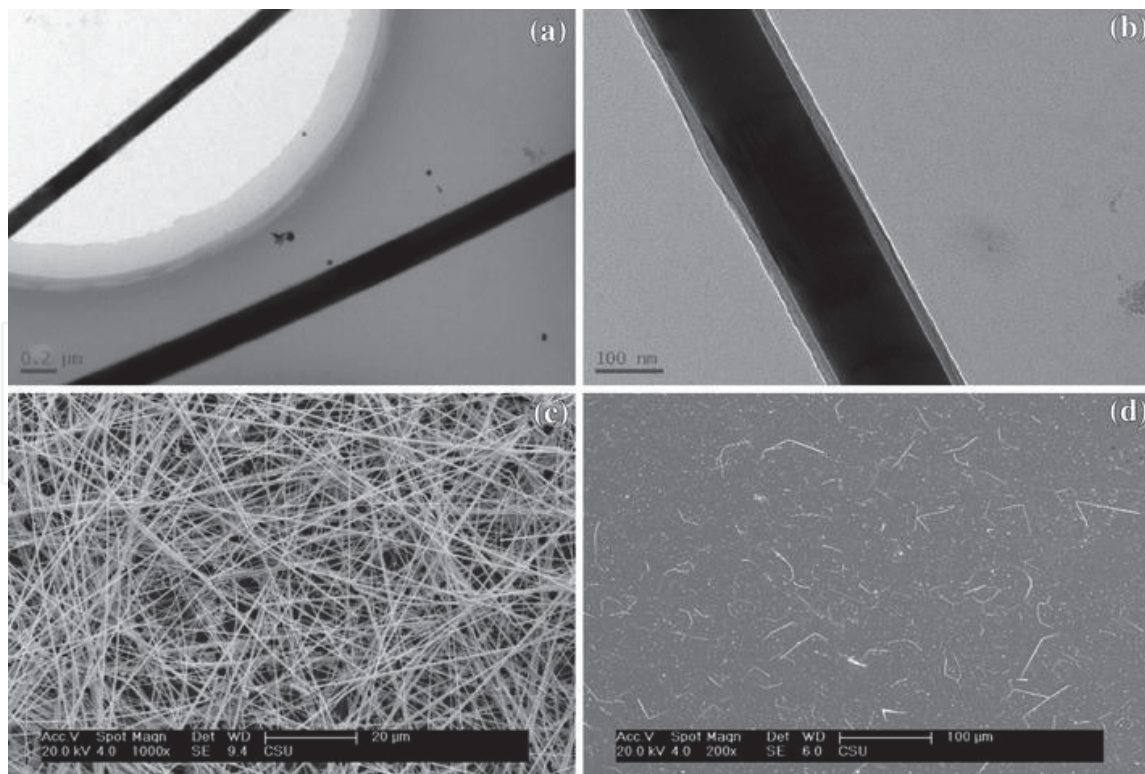


Figure 10. (a) TEM image of core-shell structured AgNW. (b) TEM image of an individual AgNW. (c) SEM image of core-shell structured AgNW. (d) SEM image of AgNW/PI hybrid film [35].

than the maximum discharge energy density of the equivalent single-layer composite film (1.5 J cm^{-3} , at 210 kV mm^{-1}); at a high electric field of 300 kV mm^{-1} , the t-KPI composite film could still maintain 88% charge and discharge efficiency [36]. Amin Azizi et al. [37] prepared large-scale high-quality hexagonal boron nitride (h-BN) films using vapor deposition technology (CVD) and transferred them to PEI films to synthesize h-BN/PEI/h-BN composite film. As shown in **Figure 11**, this composite film exhibits excellent charge-discharge efficiency and dielectric stability at high temperatures. At 100°C , the discharge energy density of h-BN-coated PEI reached 2.93 J cm^{-3} , and its charge-discharge efficiency was $>90\%$. As the operating temperature increased, its advantages become more obvious. At 200°C , the energy density of h-BN-coated PEI film was 1.19 J cm^{-3} . Rapid cyclic discharge experiments were performed at 150°C and 200 MV m^{-1} to test the stability of h-BN/PEI/h-BN composite films under electric fields and high temperature. The results demonstrated that the h-BN/PEI/h-BN film coated with 19 layers of h-BN did not show any reduction in discharge energy density and charge-discharge efficiency over 55,000 charge-discharge cycles [37].

Chen et al. [38] prepared an amino-modified CNT/PI ($\text{NH}_2\text{-MWCNT/PI}$) flexible composite film with a three-layer structure in which a high-dielectric $\text{NH}_2\text{-MWCNT}$ was inserted between pure PI layers (serving as the bottom and top layers) of the complex. Since the conductive paths of the insulating layer could be effectively isolated, the three-layer composite film showed high ϵ_r and low dielectric loss. It is worth noting that at 1 kHz, when the $\text{NH}_2\text{-MWCNT}$ content of the intermediate layer was 10 wt%, the multilayer composite film (P-10-P) gave the highest ϵ_r of 31.3, while the dielectric loss was 0.0016. In addition, the maximum energy density of the composite membrane containing 5 wt% $\text{NH}_2\text{-MWCNT}$ in the intermediate layer (P-5-P) was as high as 1.95 J cm^{-3} , which is more than 50% higher than that of pure PI (1.41 J cm^{-3}). The maximum energy density of the composite film P-10-P also remained at 1.31 J cm^{-3} [38]. Among the various films,

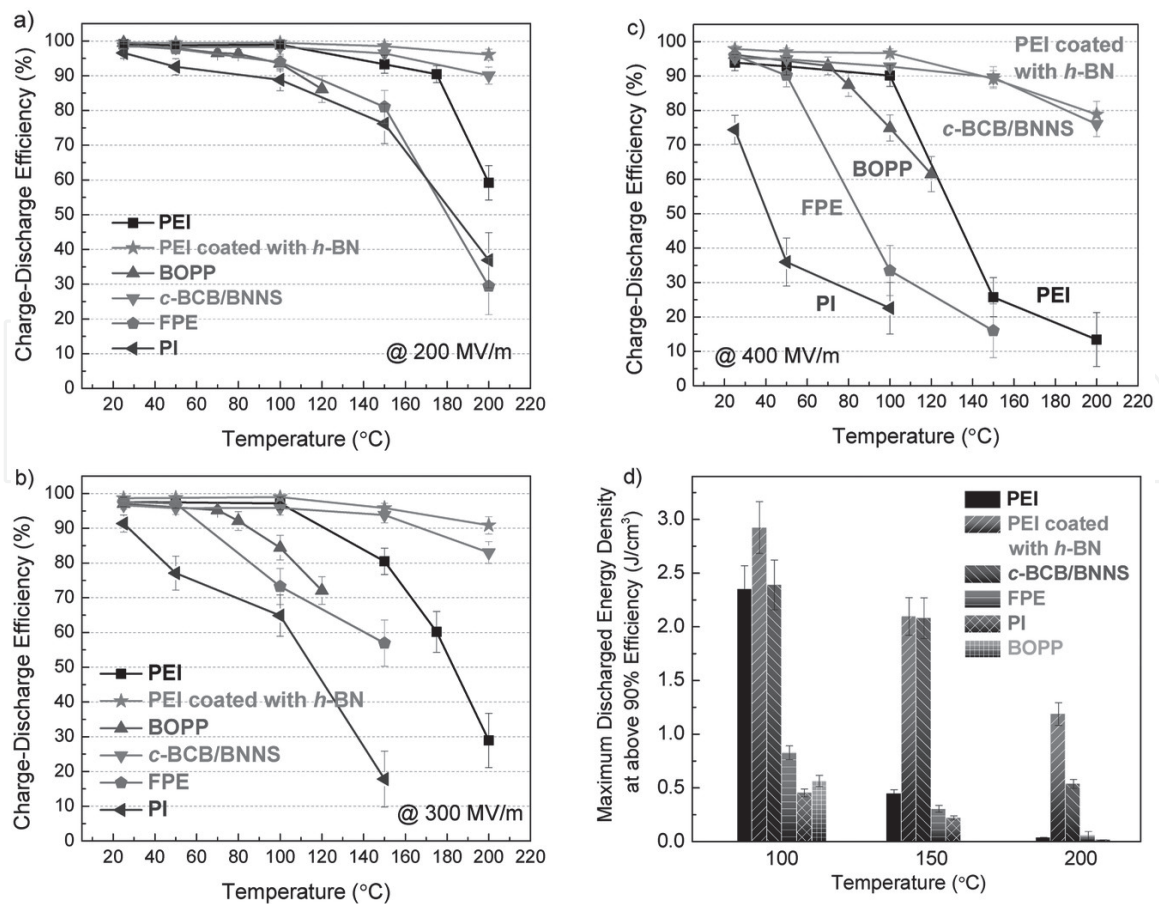


Figure 11.

Charge-discharge efficiency of the dielectrics as a function of temperatures measured at an applied field of (a) 200, (b) 300, and (c) 400 MVm^{-1} . (d) Discharged energy density achieved at above 90% charge-discharge efficiency at varied temperatures [37].

h-BN/PI composite film filled with 5 vol% h-BN as the outer layer could improve the heat dissipation ability of the three-layer composite material, thereby maintaining the dielectric strength and suppressing leakage current at high temperatures. Hence, this sandwich structure composite material had excellent energy storage properties and high temperature stability. At 25 and 150°C, the maximum field strengths of the composite film with a Zr and Ca modified BT (BZT-BCT) content of 1 vol% in the intermediate layer were 360 and 350 kV mm^{-1} respectively, while the storage densities were 2.3 and 1.83 J cm^{-3} , respectively [39]. Zhou et al. [40] proposed a method for preparing high-performance polymer dielectrics at high temperatures (designed roll-to-roll plasma enhanced CVD), which was easily adapted to large-scale production of various surface-functionalized polymer films. In this experiment, they uniformly deposited wide-band gap SiO_2 on the dielectric polymer film at ambient temperature and atmospheric pressure, and their productivity was comparable to that of melt extrusion. The results showed that the introduced SiO_2 layer increased the potential barrier at the electrode/dielectric interface, resulting in a significant decrease in conductivity. Therefore, compared with the pure polymer (see Figure 12), the SiO_2 -coated film exhibited good high-temperature capacitance performance and had a higher energy storage efficiency (η) value. For example, at 150°C, when $\eta > 90\%$, the maximum U_e values of PEI- SiO_2 , PEN- SiO_2 , PI- SiO_2 , PC- SiO_2 , and FPE- SiO_2 composite films were 2.12, 1.75, 1.24, 1.79, and 2.06 J cm^{-3} , which were respectively 236, 672, 510, 1279, and 644% greater than the corresponding pure films. At 100°C, when $\eta > 90\%$, U_e for PEI- SiO_2 was 3.0 J cm^{-3} [40].

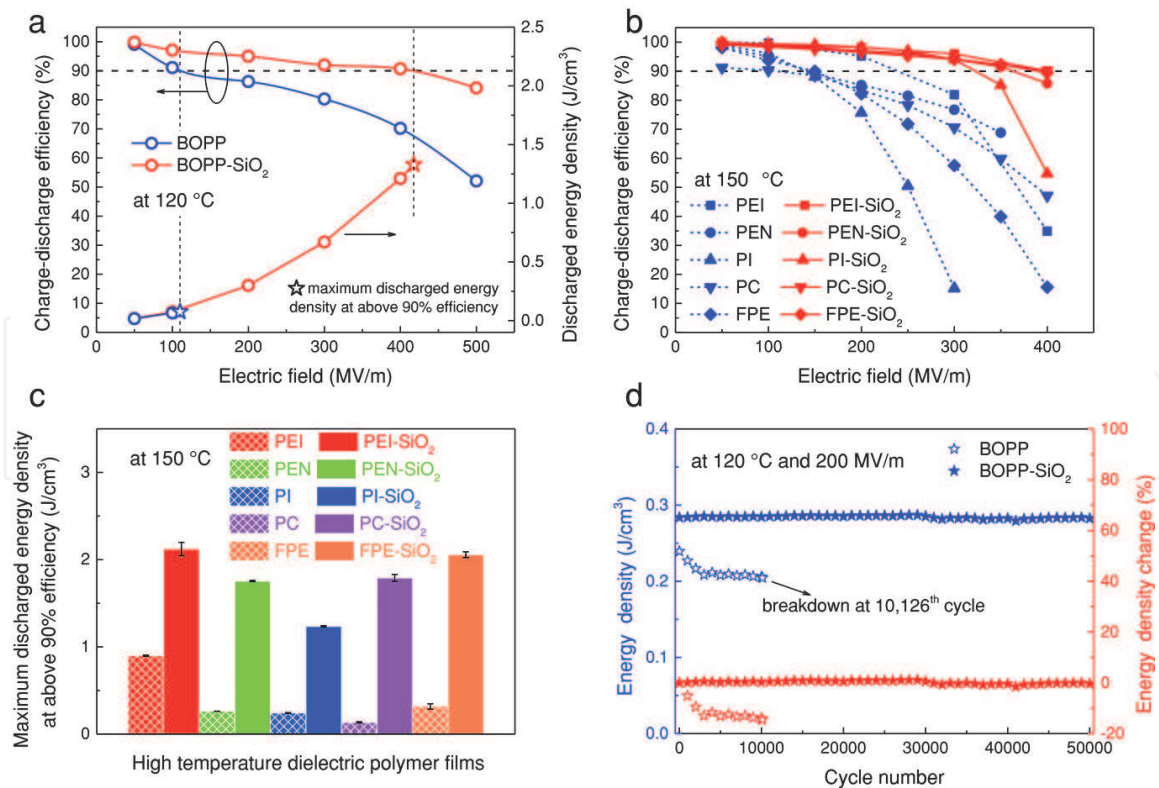


Figure 12. (a) Charge-discharge efficiency and discharged energy density of BOPP and BOPP-SiO₂ films with 180 nm coating layer on each side of the polymer measured at 120°C . (b) Charge-discharge efficiency of the various dielectric films before and after coating measured at 150°C . (c) Maximum discharged energy density of the various dielectric films before and after coating achieved at above 90% charge-discharge efficiency measured at 150°C . (d) Discharged energy density obtained from cyclic fast discharge tests of pristine BOPP and BOPP-SiO₂ films [40].

5. Conclusion

In conclusion, the high-temperature polyimide dielectric materials used in energy storage application have been summarized, including pure PI, structure modification of PI, PI-based nanocomposites, etc. Many methods for micro molecule dimension and macrostructure design have been analyzed. The reviewed research studies encompassed commercial products progress, material design, and specification, the fundamental theory such as dielectric properties, energy density, and thermal properties. However, the current research for available high-temperature dielectric materials still falls short of industrial application, especially operating under extreme environment conditions, due to the relatively low dielectric permittivity and higher dielectric loss, which severely limit the energy storage density. Moreover, the thermal conductivity is also a limiting factor for high-temperature polymer dielectric materials. Therefore, more fundamental research on developing high-performance intrinsic polymer and high-temperature dielectric phenomena should be focused for future application.

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Conflict of interest

The authors declare no conflict of interest.

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Author details

Jun-Wei Zha^{1*}, Xue-Jie Liu¹, Yaya Tian¹, Zhi-Min Dang² and George Chen^{3*}

1 School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing, P.R. China

2 Department of Electrical Engineering, Tsinghua University, Beijing, P.R. China

3 School of Electronics and Computer Science, University of Southampton, Southampton, United Kingdom

*Address all correspondence to: zhajw@ustb.edu.cn and gc@ecs.soton.ac.uk

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