

Review Article

Polyarylene Ether Nitrile-Based High- k Composites for Dielectric Applications

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Flexible polymer-based composites exhibiting high dielectric constant as well as low dielectric loss have been intensively investigated for their potential utilization in electronics and electricity industry and energy storage. Resulting from the polar -CN on the side chain, polyarylene ether nitrile (PEN) shows relatively high dielectric constant which has been extensively investigated as one of the hot spots as dielectric materials. However, the dielectric constant of PEN is still much lower than the ceramic dielectrics such as BaTiO₃, TiO₂, and Al₂O₃. In this review, recent and in-progress advancements in the designing and preparing strategies to obtain high- k PEN-based nanocomposites are summarized. According to the types of the added fillers, the effects of organic fillers, dielectric ceramic fillers, and conductive fillers on electric properties of PEN-based composites are investigated. In addition, other factors including the structures and sizes of the additive, the compatibility between the additive agent and the PEN, and the interface which affects the dielectric properties of the obtained composite materials are investigated. Finally, challenges facing in the design of more effective strategies for the high- k PEN-based dielectric materials are discussed.

1. Introduction

Designing and fabrication of novel advanced electronic materials feeding for the rapid development of information technology has attracted considerable attention for their applications as integrated and portable electronic devices [1, 2]. Miniaturization, portability, and high performance of these materials are the guiding directions for the development of highly integrated components [3–6]. Capacitor, as an important energy storage device, is the most common electronic devices fabricated by dielectrics with high- k , high breakdown strength, high-energy density, but low loss tangent [7, 8]. Among these parameters, relative permittivity and loss tangent are the most significant ones which can be easily obtained by researchers and/or manufacturing workers to evaluate the final properties when used in electronic and electrical applications [9–11]. Traditional dielectric materials include oxides (ZnO, Al₂O₃, etc.) [12, 13] and ferroelectric ceramic materials such as (TiO₂, BaTiO₃, etc.) [14, 15]. The dielectric constant of oxides is generally below 50, which is not high enough to be used in capacitors. In comparison,

the dielectric constant of ferroelectric ceramics can be as high as 10⁴ with extremely low dielectric loss and excellent thermal stability, which meets the requirements of most application devices [16, 17]. These ferroelectric ceramic dielectrics exhibiting relatively higher permittivity have attracted tremendous research enthusiasm because of their applications as power transmission system, high-energy storage capacitor, microwave communication, and so on [18–20]. However, to fulfil demands from the electronic industry, it is still a challenge with critical importance to fabricate lightweight and portable equipment with these inorganic dielectric materials. First of all, the density of inorganic materials makes it difficult to meet the requirements of lightweight and portable devices. Secondly, most inorganic dielectric materials require high sintering temperature, which is not conducive to the preparation of materials, energy conservation, and environmental protection. Thirdly, it is difficult to realize the bending and flexibility of large curvature due to the structural characteristics of the inorganic material. Finally, the poor corrosion resistance to acid and alkali limits its application in some special fields [21–23].

In comparing with the inorganic materials, high-performance polymers and polymer-based composites (organic materials) show the characteristics of lightweight, flexibility, and resistance to acid and alkali as well as easy processing [24, 25]. As a result, these organic materials are tremendously studied as dielectrics to replace the inorganic materials [26–28]. However, the relatively low permittivity of polymer limits its further utilization as dielectrics. Fortunately, the relative permittivity of the polymer can be effectively improved through the introduction of fillers [24]. At present, the fabrication of polymeric composite dielectrics showing high- k , low loss tangent, low density, and good mechanical properties is of great significance to the preparation of new energy storage elements [25].

The polymer-based composites are two component, three component, and/or multicomponent [29, 30] mixtures consisting of polymer matrix and additives. As for the polymer matrix, polymeric dielectric materials are widely used in various fields of social production and life resulting from their easy processing and high dielectric strength. Up to now, polyimide (PI), polyethylene (PE), and polyvinylidene fluoride (PVDF) as well as many other polymers have been employed to fabricate capacitors [31–34]. However, resulting from their relative low T_g , the polymeric dielectrics including PE and PVDF cannot work continuously at atmospheres higher than 160°C. The present solution, which uses additional thermal management systems to cool the devices, is impracticable in low-cost and large-scale applications. As a result, candidates with higher T_g are imperative [35]. Polyarylene ether nitrile (PEN), a high-performance thermoplastic polymer, has been intensively studied because of its excellent performances including thermal stability, easy processing, radiation resistance, and excellent mechanical performances as well as chemical resistance [36–38]. In addition, resulting from the polar -CN on the side chain, PEN shows relatively high dielectric constant. Basing on these novel properties, PEN has shown its application as dielectrics at high-temperature environments in automotive and electronic industries [39, 40].

In order to obtain composites having high permittivity, various kinds of fillers, including ferroelectric ceramics, conductive nanoparticles, and organic dielectrics, are incorporated into the polymer matrix [41, 42]. Usually, the higher permittivity of the used additives, the better permittivity of the obtained composites [14, 17]. As a result, the most used additives include the high-permittivity ferroelectric ceramics and the conducting fillers [15, 16, 30]. Maxwell-Wagner polarization indicates that the permittivity of the composite increases obviously when the content of the filler reaches a critical value (percolation threshold) [14]. Unfortunately, the loss tangent of the system increases simultaneously due to the incompatibility between the organic substrate and the inorganic additives. As a result, the micromorphology of fillers, the distribution mode of the additives in the polymeric substrate, surface treatment, and preparation methods of the fillers (i.e., “core-shell” nanoarchitectures) [43–46] are equal important as the kind of fillers that determines the properties of the obtained composites [47–51]. This article reviews the progress of PEN-based composites exhibiting

high- k for electric applications. Furthermore, the feasible methods to improve permittivity and reduce loss tangent of the composites are emphatically analyzed.

2. PEN Matrix

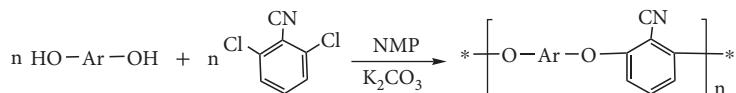
At present, some kinds of polymer dielectric materials such as biaxial tensile polypropylene and polyester are used in civil fields. Although they have shown excellent dielectric properties, these dielectric materials can only maintain the stability of various performance under 160°C [52, 53], which is far from meeting some high-tech applications, such as aerospace and new energy vehicles. Therefore, the high- k material with high thermal stability has aroused the interest of researchers. It is well known that PEN is a high-performance thermoplastic engineering resin owing to the high mechanical behavior, thermal stability, easy processing, radiation resistance, and corrosion resistance [54–58].

PEN matrix was usually prepared via the reaction of nucleophilic substitution polymerization synthesized by 2,6-dichlorobenzonitrile and aromatic diphenols under the catalysis of potassium carbonate, which has widely reported in previous work [54]. The associated synthesis route is shown in Figure 1. It can be seen the strong polarity group of -CN in the side of macromolecular chain of PEN, and the main chain contains a large number of rigid aromatic rings. In addition, there is a free rotational -O- (ether bond) in the main chain. Therefore, these characteristics endow the PEN with excellent tensile strength, tensile modulus, chemical stability, and radiation resistance [56]. The performance parameters of the first industrial PEN ID-300 [59] are shown in Table 1.

Besides, with the development of polymerization methods, the PEN is not limited to the homopolymer of PEN mentioned above. Professor Liu's group has prepared a series of random copolymers and block copolymers of PEN [60], which greatly enriches the variety of PEN meeting different application requirements of the modern society. What is more, with nearly 40 years of development, the series of PEN can be divided into amorphous PEN, semicrystalline PEN, and crystalline PEN according to its crystallinity, and it can also be divided into noncross-linked PEN and cross-linked PEN according to the cross-linking of the system.

3. High- k PEN Composites

High permittivity of the materials is the basic property for their application as capacitors. Although the ceramic material exhibits high- k , it is also hard to suit current requirements for the development of energy storage elements. The development of polymer-based composite containing polymer matrix and additives as dielectric material is one of the technical routes to solve this problem. Combining flexibility and lightweight of polymer matrix with high- k of additives, the polymer-based composites are endowed with specific properties, such as high- k , lightweight, and easy-to-process [61, 62]. On the basis of the type of additives, the polymer composite dielectric materials were divided into polymer-



where representative–Ar–can be any of these groups:

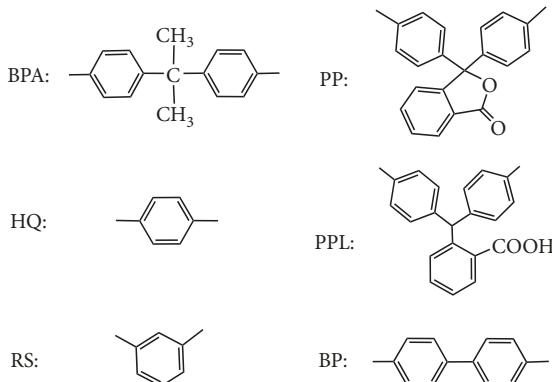


FIGURE 1: Synthesis route of PEN.

TABLE 1: Properties of PEN ID-300.

Product property	Performance parameter
Thermal properties	Glass transition temperature (T_g) is 145°C; hot deformation temperature is 165°C; continuous use temperature is 230°C
Mechanical properties	Tensile strength is 123 MPa; breaking elongation is 15%; tensile modulus is 2.3 GPa
Dielectric properties	Dielectric constant is about 3.5; dielectric loss is 0.08–0.01 (1 kHz)
Corrosion resistance	Resistance to organic solvents, alkaloids, ketones, and hydrocarbons excepted sulfuric acid

based composite dielectric materials filled with organic fillers, ceramic fillers, conductive fillers, among others.

3.1. High-*k* PEN Composites with Organic Fillers. The advantage of organic filler is that it exhibits good compatibility with polymer matrix and is easily to be dispersed uniformly in PEN matrix to obtain homogenous composite material. The organic filler/PEN composite dielectric materials show excellent mechanical properties and are suitable for preparation of composite thin film with high-*k*. Phthalocyanines (Pcs) have highly coplanar 18 electronic π -bonded conjugate structures and can react with a number of metal ions to form metal phthalocyanine (MPcs), as shown in Figure 2. Meanwhile, the axis and edge of phthalocyanine ring can connect many kinds of special functional active substituent, its structure modification makes these compounds with physical and chemical properties [63]. As a classic organic semiconductor, the dielectric constant of copper phthalocyanine (CuPc) is up to 10^5 [64]. The dielectric permittivity and loss tangent of PEN/CuPc nanocomposite materials are about 45 and 0.4 at 1 kHz, respectively [65]. When the filler mass fraction of CuPc is up to 40 wt%, the PEN/CuPc composites still maintain good mechanical properties. In addition, the

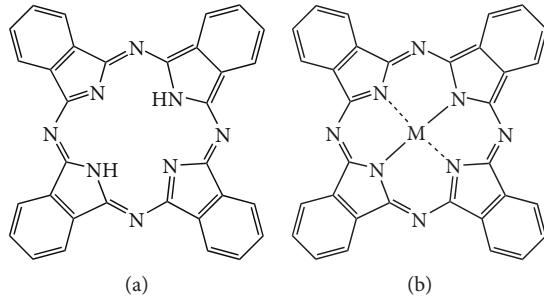


FIGURE 2: Structures of phthalocyanines (a) and metal phthalocyanines (b).

surface treatment of CuPc by chemical modification is an effective way to improve the dispersion of fillers and polymer, decrease the dielectric permittivity-frequency dependence, and reduce the loss tangent of the composites significantly. On the other hand, phthalocyanine-containing polymers, prepared by self-polymerization and/or self-assembly of Pcs, not only possess the unique physical and chemical properties of Pcs, but also combine good solubility and processability of polymers [66].

Beside the Pcs, organic compounds which can form Pc after cross-linking are also introduced into PEN matrix to make PEN composites. Yang et al. [67] prepared 1,3,5-tri-(3,4-dicyanophenoxy) benzene (TPh) through a reaction with the phloroglucinol and 4-nitro-phthalonitrile and then prepared the PEN/TPh composite materials which presented high dielectric permittivity, low loss tangent, and high heat resistance. Furthermore, the phthalocyanine rings can be formed by self-cross-linked through the -CN group in pendants or in the end of macromolecular chain of PEN [68], which can improve the dielectric properties and thermal stability of the composites. As shown in Figure 3, when PEN matrix was mixed with TPh, the dielectric permittivity of the obtained samples after cross-linking at high temperature is much higher than that of films without cross-linking. It is

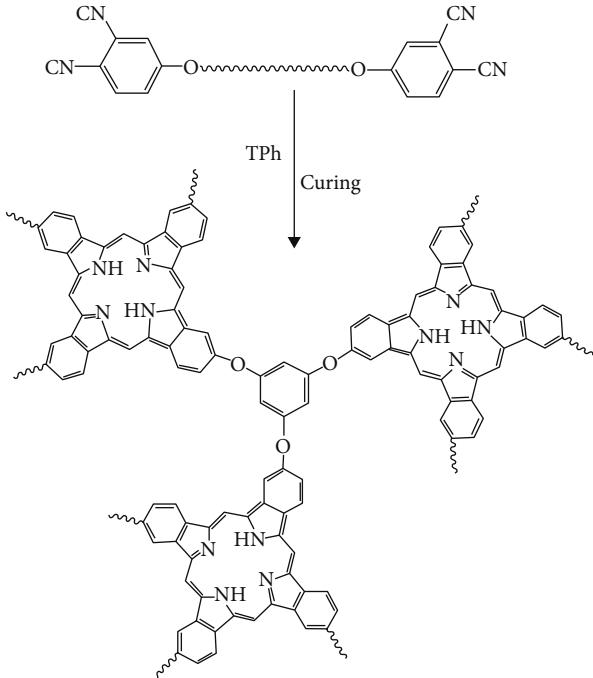


FIGURE 3: Formation of phthalocyanine rings from PEN and TPh.

because that the phthalocyanine rings were formed during the cross-linking which increased the dielectric permittivity of the samples. Besides, the formation of cross-linking network contributed to the low loss tangent. More importantly, the microscopic structures of the obtained PEN/TPh system have a big change after self-cross-linking, and the homogeneous phases were formed gradually from phase separation. The properties above make the PEN/TPh composites show a great potential for application in some extreme environment [67].

High- k polymers can be also treated as fillers to increase the dielectric properties of polymers. Long et al. [69] reported that the polyvinylidene fluoride (PVDF) and PEN polymer alloys with different mass ratios were prepared successfully by solution casting method. For PVDF/PEN alloy (with 90 wt% PVDF), it can be seen that the dielectric permittivity has a slight decrease from 7.1 to 5.8 (1 kHz) with the frequency from 25 Hz to 1 MHz, which presented a weak dependence of dielectric constant and frequency. Besides, it is also found that the dielectric permittivity and loss tangent of PVDF/PEN alloy (with 90 wt% PVDF) increase slowly from 7 and 0.02 to 18 and 0.05 (1 kHz) before the melt point of PVDF, which indicated that the PVDF/PEN alloys have a relatively stable dependence of dielectric permittivity and temperature.

Moreover, the organic conducting polymeric materials are also used as additives to fabricate high- k polymer-based composite materials. Wei et al. [70] investigated that the polyaniline (PANI) was doped with sulfuric acid as a filler to prepare PEN/PANI composite films for improving the dielectric permittivity of PEN by using solution casting method. It is clearly seen that there was just a T_g of the composites on DSC curves, and no phase separation was observed on the SEM images. All these indicated that the PANI has a

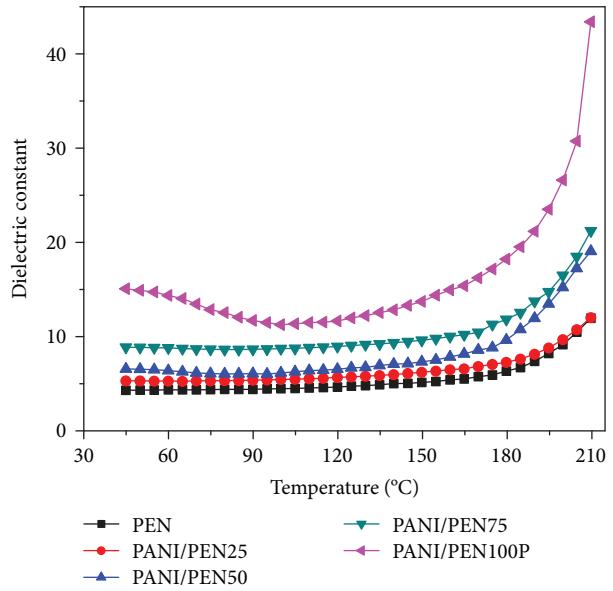


FIGURE 4: Dielectric permittivity-temperature dependences of PEN/PANI composites at 1 kHz. (PEN, PANI/PEN25, PANI/PEN50, PANI/PEN75, and PANI/PEN100 represent the composites with 0, 2.5, 5.0, 7.5, and 10 wt% of PANI, resp.).

well compatibility with the PEN matrix. Besides, the dielectric permittivity of PEN-based composite film presented a sostenuto increase with the increment of PANI content. When the content of PANI is 10 wt%, the dielectric permittivity of the PEN/PANI composite film is 23.5 at 250 Hz, which increases by 650% by comparing to pure PEN matrix. The dielectric properties indicated that the PANI can enhance the dielectric permittivity of PEN effectively. In addition, the PEN/PANI composites have a relatively stable dependence of dielectric permittivity and temperature before 180°C (Figure 4).

3.2. High- k PEN Composites with Ceramic Fillers. Apart from organic fillers, selection of high- k dielectric ceramic fillers of different types and shapes improves the dielectric permittivity of PEN-based composites effectively. It is well known that the dielectric permittivity of ferroelectric ceramics can be as high as 10^4 with extremely low dielectric loss and excellent thermal stability. PEN-based composites with high- k are easily prepared after the incorporation of these ferroelectric ceramics. However, due to the poor compatibility between the polymer matrix and the fillers, the loss tangent of the composites will increase dramatically without modification. As a result, the micromorphology of fillers, the dispersion mode of the fillers in resin matrix, surface treatment, and preparation methods are equal important as the kind of fillers that affect the dielectric properties of PEN composites.

3.2.1. Ceramic Nanoparticles as Fillers. The mostly used high- k ceramics are barium titanate (BaTiO_3) [41], strontium titanate (SrTiO_3) [71], titanium dioxide (TiO_2) [14], calcium titanate (CaTiO_3) [72], among others. Ceramic additives serve as insulators due to high bandgap, and accumulation

of charges can only take place under a certain electric field. Besides, it is crucial for the improvement of the dielectric constant of polymer-based composites in interfacial area between the polymer matrix and fillers. What is more, the dielectric permittivity of the ceramic additives is much higher than the resin matrix, and the dielectric permittivity of polymer-based composites is enhanced with the increment of the filler content which leads to an increment in the interfacial area of polymer matrix and fillers [73]. Especially, the relationship between dielectric permittivity and filler content is increasing linearly. As a result, the content and size of ceramic particles are two important matters affecting the electrical characteristics of the obtained polymer-based composites [74].

(1) *Effect of Filler's Content.* Every barber knows that the dielectric permittivity of the polymer-based composites increases with the increase of ceramic filler content. Hence, the dielectric permittivity of polymer matrix can be obtained 10–20 times by filling in high-proportion ceramic particles (>50%, volume fraction). Tang et al. [75] reported that the PEN/BT nanocomposites were prepared through the ultrasonic dispersion fabrication process. The dielectric constant of PEN/BT nanocomposites increased from 4.07 to 12.55 at 1 kHz with the content of BT nanoparticles increased from 0 wt% to 40 wt%. Besides, although the dielectric permittivity of the PEN-based nanocomposites decreases with the increase of frequency, the dependence of the frequency and dielectric permittivity is reduced. However, the high content of ceramic fillers will make the particles unfavorable to uniform dispersion in the resin matrix, which leads to the agglomeration of the additives and formation interfacial voids and pores [76]. This would drastically reduce the mechanical strength and breakdown strength of polymer-based composites. Therefore, the breakdown strength of PEN/BT nanocomposites decreased rapidly from 231.48 to 158.07 kV/mm with the content of fillers increased from 0 wt% to 40 wt%.

(2) *Effect of Filler's Size.* The size of filler is another important factor affecting electrical properties of ferroelectric ceramics/polymer composites. Besides, the performance of particle has a close relationship with the filler's size, which is usually presented as the smaller the filler's size is, the larger the specific surface area is. When additives with micron size or larger are introduced into polymer matrix, defects are easily formed which results in the electric field distortion in composite materials. At the same time, the local electric field will be enhanced by the void and porosity caused by agglomeration of the additives in the polymer-based composites. All these defects reduce the breakdown strength and mechanical strength of the composites. In comparison, the nanosized filler can effectively enhance mechanical properties of polymer-based composites and increase the amount of the ceramic fillers filled in the matrix. Theoretically, the dielectric permittivity of polymer-based composites increases with the decrease of filler particle size. It is mainly because that the use of small particle size fillers will increase the interface area among polymer resin and filler, which enhanced

interface polarization causing by the increment of the electron density on the interface [77, 78].

3.2.2. Core-Shell-Structured Ceramic Nanoparticles as Fillers. Dispersion and compatibility of fillers within the polymer substrate are the most important parameters that determine the dielectric properties of the polymer-based composites. When the additives are heterogeneously distributed within the polymeric substrate, defects and voids which obviously reduce the mechanical strength and dielectric constant of the system emerge easily. As the PEN contains oleophilic groups, while the surfaces of fillers tend to have hydrophilic groups, such as -OH and -COOH, it is extremely easy to produce local reunion causing by incompatibility of them when the filler is blended with the polymer matrix directly. As a result, there are still some challenges before achieving desirable composites even although the use of nanoparticles shows some advantages in designing high-permittivity polymer composites. These challenges include achieving homogeneous dispersion, tailoring the nanoparticle interface within polymer matrix, among others, which are the key points to realize composites with desired dielectric property. In order to solve these problems, the fabrication of core-shell-structured particles with organic shells is usually adopted.

(1) *Core-Shell-Structured Ceramic Nanoparticles.* Polymer-based nanocomposites with high- k have shown application as dielectrics in energy storage due to their intrinsic properties including lightweight and easy processing. To achieve applications of the additives in enhancing dielectric properties of the system, many researchers prepared core-shell-structured additives, which are effective tool for the fabrication novel high-permittivity polymer-based composites [43]. At the early stage, many surfactants, oligomers, and small molecules were used to improve the compatibility of the two-phase interface by using the weak electrostatic interaction between molecules or van der Waals force to form a shell layer [79, 80]. However, at the filler's surface, the physical adsorption of these molecules cannot form a stable interface, resulting in the low dielectric strength and high dielectric loss. Therefore, stronger forces such as chemical bond and/or hydrogen bond, through which a more stable interfacial layer can be formed between the inorganic additive and the polymeric substrate, are needed. Generally, the introduced chemical bond not only reduces the defects at the interface, but also improves the physical property of the system. What is more, the chemical bond between the interfaces can keep the composites stable in the electric field and force field. In addition, phase separation is effectively stopped with the existence of chemical bond between additives and polymeric substrate [81].

Taking BaTiO₃ as a representative, Figure 5 presents a general method in preparing high-permittivity polymer composites using core-shell-structured additives. Combining the rotary coating technology with a posttreatment bonding process, Tang et al. [82] reported a new method to prepare BaTiO₃@CPEN core-shell-structured nanoparticles. The CPEN shell is carboxyl-functionalized polyarylene ether nitrile on which the carboxyl groups react with the hydroxyl

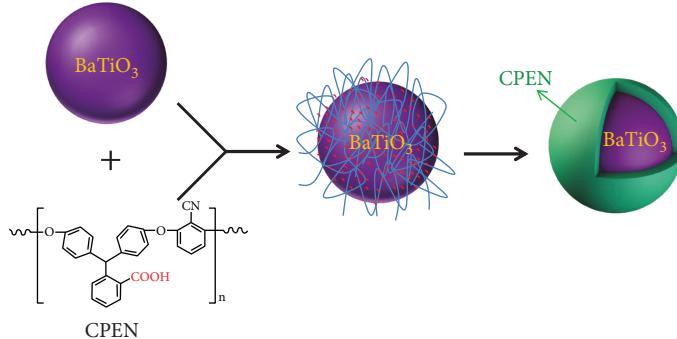


FIGURE 5: Synthetic route for the core-shell-structured BaTiO_3 /CPEN nanoparticles.

groups on the surface of BaTiO_3 . The TEM results showed that the BaTiO_3 core was wrapped by the CPEN shell completely, and the thickness of the CPEN shell was in the range of 4–7 nm. Then, the $\text{BaTiO}_3@\text{CPEN}$ and PEN composite films with different contents of $\text{BaTiO}_3@\text{CPEN}$ were fabricated through the solution casting method. The dielectric permittivity of pristine PEN is 4.3, while it gradually raises with the addition of $\text{BaTiO}_3@\text{CPEN}$. When the content of $\text{BaTiO}_3@\text{CPEN}$ is 40 wt%, the dielectric permittivity of the obtained composite is as high as 13.5, which is about 3 times compared with the PEN. The dielectric loss increases a little with the addition of $\text{BaTiO}_3@\text{CPEN}$, but it keeps lower than 2.3% even plenty of additives were added. It is because that the CPEN shell at $\text{BaTiO}_3@\text{CPEN}$ has the similar structure with the PEN substrate, the compatibility between the CPEN and PEN results in the homogeneous dispersion of $\text{BaTiO}_3@\text{CPEN}$ in PEN substrate which decreases the interfacial polarization, and thus, a low dielectric loss system was obtained. Similarly, Huang et al. [83] prepared a series of surface-modified titanium dioxide ($\text{TiO}_2@\text{CPEN}$) and PEN composites with different mass contents of $\text{TiO}_2@\text{CPEN}$ by using a similar method. TiO_2 nanoparticles were completely wrapped by CPEN and formed the core-shell structures. The modified TiO_2 nanoparticles were uniformly distributed in the PEN substrate due to the existence of the CPEN shell. Moreover, the $\text{TiO}_2@\text{CPEN}$ particles did not display any signs of evulsion in the PEN substrate, resulting from the fact that the interaction between PEN and the interface of $\text{TiO}_2@\text{CPEN}$ particles is quite strong. The result indicated that permittivity of the $\text{TiO}_2@\text{CPEN}/\text{PEN}$ composite increases linearly with the increasing content of surface-modified TiO_2 particles. When $\text{TiO}_2@\text{CPEN}$ nanoparticle content is 40 wt%, permittivity of the obtained $\text{TiO}_2@\text{CPEN}/\text{PEN}$ nanocomposite at 1 kHz reaches 7.9, while loss tangent of the system is also below 3% (1 kHz).

(2) *Core-Shell-Shell-Structured Ceramic Nanoparticles.* At present, “molecular bridge” is the main method to realize the dispersion of the core-shell-shell-structured filler in the polymer substrate. The key point of the “molecular bridge” is the introduction of the inner shell acting as the buffer layer connecting both the core and the external shell. The buffer layer acts as molecular bridge forming bonds between inorganic and organic polymers. Comparing with physical adsorption, this kind of modification has better effect and

can effectively reduce the agglomeration of inorganic additives in the polymeric substrate. The mostly used buffer layer is silane coupling agent, which is a kind of low molecular organosilicon compounds with special structure [84]. Other functional materials such as carboxyl-functionalized polymers and sulfonyl-functionalized polymers are also widely used as the buffer layer [85].

Tang et al. [84] reported the preparation of core-shell-shell-structured nanoparticles $\text{BaTiO}_3@\text{SiO}_2@\text{HBCuPc}$ and then fabricated its composites with PEN as substrate. $\text{BaTiO}_3@\text{SiO}_2@\text{HBCuPc}$ was obtained by reaction between hyperbranched copper phthalocyanine (HBCuPc) and $\text{BaTiO}_3@\text{SiO}_2$ which were prepared through surface modification of BaTiO_3 with silane coupling agent KH550. What is more, combining the coating with bonding technology, You et al. [85] reported the preparation of core-shell-shell-structured nanoparticles $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}$ with carboxyl-functionalized polyarylene ether nitrile (CPEN) as the buffer layer. The preparation of $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}$ nanoparticles is shown in Figure 6. In the first step, the BaTiO_3 was coated with CPEN through the interaction between the carboxyl at CPEN and the hydroxyl on the surface of BaTiO_3 . Then, the other carboxyl at CPEN reacted with the amino groups at copper phthalocyanine (CuPc). The core-shell-shell-structured nanoparticles $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}$ were incorporated into the PEN substrate to fabricate $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}/\text{PEN}$ composites. Their result showed that the permittivity of the $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}/\text{PEN}$ composites is stable in the measured frequency. When the $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}$ is 20 wt%, the permittivity of the $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}/\text{PEN}$ composite at 1000 Hz is up to 9.0, with an increment of 130% compared with that of PEN substrate. The increasing of the permittivity can be explained by the formation of microcapacitors in the composite system, and the more the additives are added, the more the microcapacitors are formed [86]. In comparing with $\text{BaTiO}_3/\text{PEN}$, $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}/\text{PEN}$ shows higher permittivity at the same content of the additive. This is because the better compatibility between $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}$ and PEN as well as the high permittivity of the CuPc. Meanwhile, the compatibility of the $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}$ with the PEN substrate contributes to the low dielectric loss. The dielectric loss of $\text{BaTiO}_3@\text{CPEN}@/\text{CuPc}/\text{PEN}$ films at 1000 Hz is only 3.1% with the nanofiller content up to 20 wt%. Another result they obtained is that the

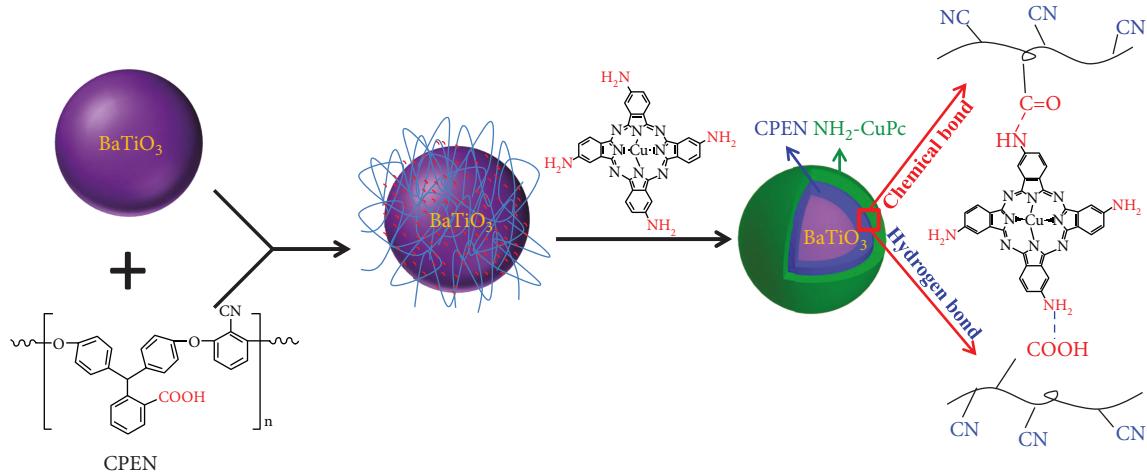


FIGURE 6: Synthetic route for the core-shell-shell-structured nanoparticles.

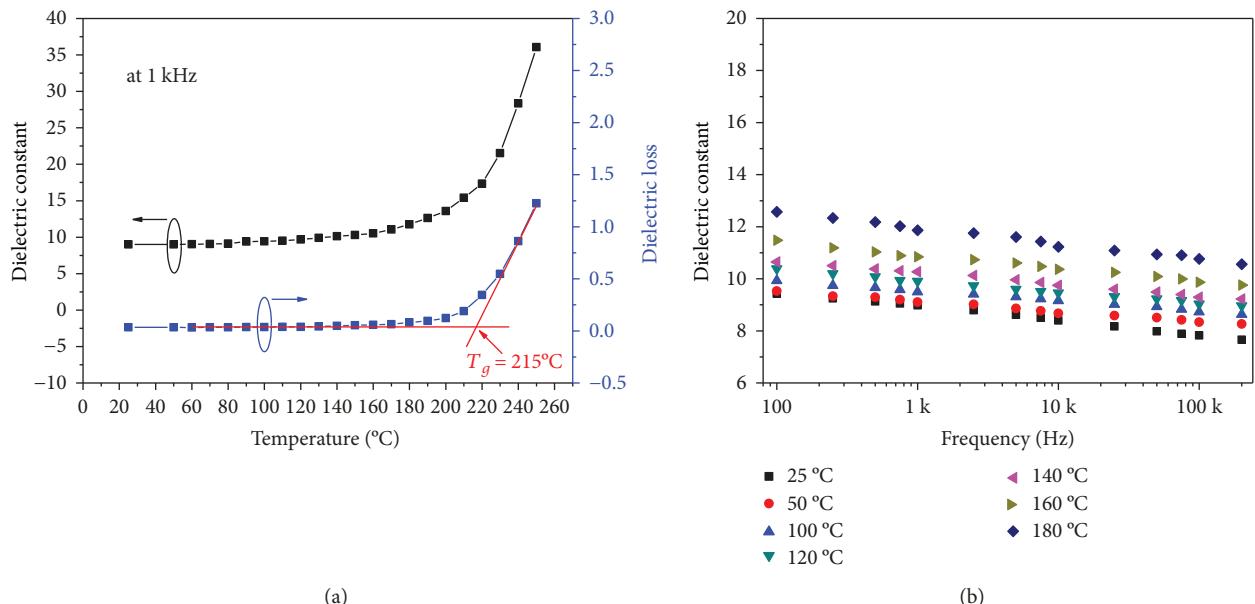


FIGURE 7: The permittivity-frequency properties of BT@CPEN@CuPc/PEN (20 wt%).

permittivity and the dielectric loss of the $\text{BaTiO}_3@\text{CPEN}@\text{CuPc}/\text{PEN}$ composite are quite stable when the temperature is lower than its T_g ($>200^{\circ}\text{C}$), while both of them increase abruptly when the temperature is nearby or even higher than its T_g . In addition, stable permittivity of $\text{BaTiO}_3@\text{CPEN}@\text{CuPc}/\text{PEN}$ composite at different temperatures ($25\text{--}180^{\circ}\text{C}$) is also observed within the measured frequency, as shown in Figure 7.

In summary, the direct recombination and “molecular bridge” are the main methods to prepare the core-shell nanoparticles. Through the fabrication of the core-shell-structured nanoparticles, it is possible to adjust the parameters such as thickness of the shell, compatibility between the additive and the polymeric substrate, interface interaction, among others, which affect the final properties of the obtained high-permittivity composites.

3.3. High- k PEN Composites with Conductive Fillers. Compared with PEN composites with dielectric ceramic fillers, which usually need larger volume fraction of filler, the dielectric constant of the composite increases obviously with the addition of less conductive filler. Usually, the more the additives are added, the more the microcapacitors are formed which increase the permittivity of the system. When the conductive additives are used as the fillers, the microcapacitors can be easily formed at a lower content of the additives. As a result, the percolation threshold of the conductive additives is achieved at lower filler volume fraction, meaning the permittivity increases easily with less conductive additives.

There are many kinds of conductive fillers. Common metal conductive particles (i.e., Ag, Ni, and Al) [87] are the mostly used additives in preparing composites with high dielectric permittivity. Besides, the conductive carbon

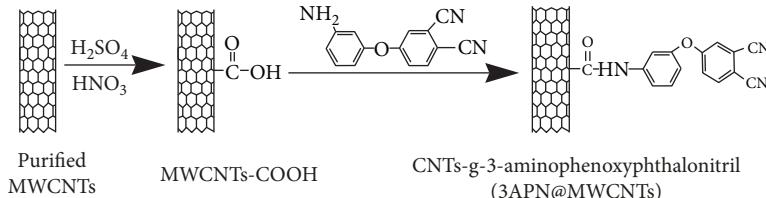


FIGURE 8: Schematic illustration of preparation of 3-APN@MWCNTs.

nanomaterials including carbon nanotube (CNT), carbon black, graphene, and graphene oxide (GO) represent another kind of widely studied conductive fillers [88, 89]. However, the volume fraction window of the composite material from dielectric to conductive material is closed to the threshold value. It is very important to control the amount of conductive fillers and to disperse them evenly. Otherwise, the conductive path will be formed locally in the material, which will increase the dielectric loss. In addition, it will also cause the energy dissipation and reduce the service life of the composites. Therefore, how to evenly disperse these conductive additives in organic polymer substrate becomes the key step in improving properties of this kind of composite materials.

3.3.1. Metal Conductive Particles as Fillers. At present, some different types of metal conductive particles have been utilized to enhance the permittivity of organic polymers [90, 91]. Through the in situ reduction of silver ion during the compositing process, Li et al. [87] reported Ag nanoparticles and PEN composite (Ag/PEN). The corresponding Ag/PEN composite films were obtained through solvent casting technique. The silver nanoparticles exhibit as nanospheres in the PEN substrate at fractions lower than 1.0 wt%, and they grow to be nanorods when more silver ion is added as the reactant. More importantly, the in situ reduced silver nanoparticles are homogeneously embedded in the PEN substrate even though the silver nanoparticles are unmodified. When 2.0 wt% of silver nanoparticles are embedded in the system, the permittivity increases to 5.8 at 1000 Hz, while the loss tangent keeps lower than 2%. What is more, with the formation of the silver nanoparticles in the system, the electric conductivity increases obviously. As less than 2.0 wt% of silver nanoparticles are embedded in the system, this kind of PEN composite can be used as antistatic materials.

3.3.2. Carbon Nanotubes (CNTs) as Fillers. Carbon nanotubes (CNTs) are monolayer or multilayer coaxial hollow tubular carbon nanotubes (CNTs) with carbon atom SP₂ hybrid bonding, forming delocalized π bonds. The conjugation effect of CNTs is remarkable. Besides, CNTs, as one-dimensional nanomaterials, exhibit fascinating properties including excellent mechanical strength, outstanding thermal conductivity, ultrahigh electrical capacity, and thermal stability [92, 93]. Due to these charming properties, CNTs have been widely adopted in substituting or replenishing traditional nanofillers to prepare composites with different functions. Zheng et al. [94] prepared composite films by using 4,4'-dihydroxybiphenyl-based PEN as the organic substrate and multiwalled carbon nanotubes (MWCNTs) as

additives. The permittivity of the obtained mixture increases from 4.3 to 6.1 (1 kHz) with the content of MWCNT fillers increases from 0 wt% to 3 wt%, exhibiting little frequency dependence with the incorporation of MWCNTs. Besides, the loss tangent of the composites increases from 0.010 to 0.026 (1 kHz) with the content of MWCNT fillers increases from 0 wt% to 3 wt%, which is caused by the incompatibility of MWCNTs with the organic PEN substrate.

Usually, the van der Waals interaction of the CNTs leads to the self-aggregation. As a result, the CNTs tend to aggregation, which impedes the enhancing of dielectric properties, rather than homogeneously distribution in the organic polymer substrate [95]. In order to overcome these defects, surface modification of CNTs and the controlling of interaction between the modified CNTs and polymeric substrate are the effective methods for the high- k polymer nanocomposites. Jin et al. [96] modified the CNT's surface by grafting organic molecules to enhance compatibility between CNT and PEN substrate. For this purpose, acidulated MWCNT was reacted with amino containing molecule 3-aminophenoxyphthalonitrile (3-APN) through solvothermal to form the modified carbon nanotube (3-APN@MWCNT) (Figure 8). After that, the modified carbon nanotube (3-APN@MWCNT) was utilized as an additive in preparing 3-APN@MWCNT/PEN nanocomposites with high permittivity. When 5.0 wt% of 3-APN@MWCNT is loaded, the permittivity of the obtained 3-APN@MWCNT/PEN nanocomposite at 50 Hz is 32.2, about 8 times to that of the PEN substrate. In addition, the loss tangent is lower than 0.9. Both permittivity and loss tangent increase linearly with the increasing of 3-APN@MWCNT at low loading. 3-APN@MWCNT shows a percolation threshold of 4.0 wt% in the system as the dielectric parameters raise obviously at higher loading. Pu et al. [97] fabricated modified CNT with phthalonitrile groups (CNT-CN) and used it as additive in preparing PEN-based composites. The CNT-CN distributed in the PEN substrate is uniformly due to the plenty of phthalonitrile groups, which are compatible with the nitriles on PEN, at the peripheral surface of it. In addition, the phthalonitriles at CNT-CN react with the nitriles on the main chain of PEN catalyzed by diaminodiphenyl sulfone (DDS) at high temperature, forming triazine rings. As a result, the permittivity can be as high as 33.9 when reacted at 320°C for 4 h.

In addition, core-shell-heterostructured CNT-based nanomaterials are also widely applied to obtain composites with high dielectric constant. Huang et al. [98] reported the preparation of core-shell-heterostructured CNT-based nanomaterials MWCNT@BaTiO₃, in which MWCNT acts as core and inorganic BaTiO₃ serves as shell, through solvothermal

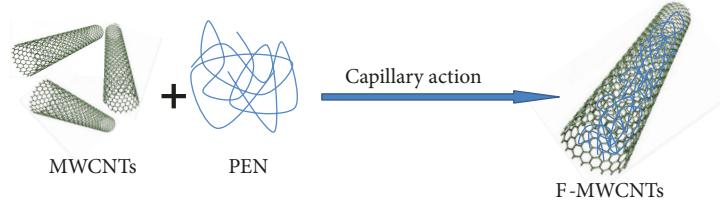


FIGURE 9: Schematic illustration of fabrication of F-MWCNTs.

reaction. After that, they fabricated MWCNT@BaTiO₃/PEN composite through solution casting. The permittivity increases to 13.8 at 100 Hz, with an increment higher than 200%, at the loading of 50.0 wt% of MWCNT@BaTiO₃. What is more, Huang et al. also prepared MWCNT@TiO₂ core-shell-heterostructured CNT-based nanomaterials via similar reaction [99]. Tetragonal anatase-phased TiO₂ clusters were formed at the peripheral surface of MWCNT. Besides acting as the additive, this core-shell-heterostructured MWCNT@TiO₂ can be used as microwave absorption materials due to its excellent electromagnetic performances.

Furthermore, You et al. [88] and Xiao et al. [100] reported the opening of MWCNTs' end offering O-MWCNTs which could be utilized as nanoscale vessels. PEN was then filled in the O-MWCNTs through capillary action to obtain F-MWCNTs (the schematic illustration of F-MWCNTs is shown in Figure 9). The PEN filled in the restricted CNT vessel shows extraordinary crystallization behavior in comparing with the crystallization at unrestricted conditions. The F-MWCNTs were also incorporated into the PEN substrate to prepare corresponding composites. The dielectric constant of PEN at 10 kHz is 4.02, and it increases after F-MWCNT is incorporated. The dielectric constant reaches 5.33 (10 kHz) for F-MWCNT/PEN when the concentration of MWCNT is 1.0 wt%. Although the dielectric losses of the composites increase with the increment of the additives, they are around 0.011. Therefore, the incorporation of the F-MWCNT into PEN is an effective approach to design dielectrics with high permittivity and low loss tangent.

3.3.3. Graphene Oxide (GO) and/or Graphene as Fillers. Graphene, a microscale 2D lattice carbon with one atomic thickness, has shown extraordinary electric property [101]. As a result, it can be used as conducting additives in the fabrication of multifunctional high-*k* polymeric dielectrics. On the other hand, graphene exhibits ultra large specific surface area of 2630 m²/g deriving from its unique structure features. Therefore, microcapacitors, which further improve the dielectric property, can be formed easily when the microsheets are isolated by the polymeric substrate in graphene-based composites. Up to now, graphene has shown its widely application in fabrication of composites with high permittivity. Wang et al. [102] prepared reduced graphene oxide (RGO) and PEN composites (RGO/PEN) through in situ thermal reduction of corresponding graphene oxide (GO) and PEN composites (GO/PEN). GO/PEN was simply fabricated by solution casting process due to the excellent dispersion of GO in solvent like NMP. After thermal reduction, GO

transfers into RGO which was uniformly distributed as that of GO in GO/PEN. When 6.0 wt% of RGO is loaded, the permittivity of the final RGO/PEN increases to 129.1 with an increment of about 2600%. In addition, the permittivity of the composite with 2.0 wt% of GO also shows a 230% increment at 50Hz when GO transforms to RGO after thermal reduction.

Similar to CNT, graphene is insoluble in most solvents due to its all-carbon composition and hydrophobic nature. It is difficult to apply on a large scale due to its poor dispersion in polymer matrixes. Therefore, it is necessary to functionalize it to change the surface energy of the graphene and thus solving the aggregation of graphene sheets in the composite [103, 104]. Up to now, the mostly utilized procedure to modify graphene is firstly disposing it with strong oxidizers to obtain GO and then reducing it back to RGO after the composting process [105–107]. Li et al. [108] prepared GO and then functionalized it with CuPc, offering GO@CuPc, through solvothermal reaction. Then, the GO@CuPc was added into the PEN substrate to prepare high-*k* nanocomposites. When 5.0 wt% of GO@CuPc was loaded in the system, the dielectric constant reaches 52.0 (at 100 Hz). Zhan et al. [109] also prepared GO and firstly reported the chemical modification of it using 4-aminophenoxyphthalonitrile (4-APN), forming (GO-CN). After that, the GO-CN was successfully introduced into PEN substrate to prepare nanocomposite films. As the phthalonitriles at GO-CN show compatibility with PEN, this route opens a new way in preparing graphene and PEN composites. What is more, Wang et al. [110] fabricated composite with GNS-Fe₃O₄ hybrid material as additive and PEN as organic substrate. The GNS-Fe₃O₄ hybrid material was prepared via solvothermal reaction from GO and FeCl₃ with ethylene glycol as the reducer.

Moreover, novel 3D CNT and graphene networks were also constructed to prevent the aggregation of them. Wei et al. [111] firstly fabricated 3D CNT-GO networks by coordinating them with metal ions (Cu²⁺, Zn²⁺, and others), forming GO-Zn-CNT. After that, a semi-interpenetrating system (GO-Zn-CNT/PEN-Ph) was obtained by penetrating a cross-linkable polyarylene ether nitrile (PEN-Ph) into the GO-Zn-CNT networks. An interpenetrating network (GS-Zn-CNT/PEN) was finally fabricated via simultaneously cross-linking of PEN-Ph and in situ thermal reduction of GO. The fabrication route for the GS-Zn-CNT/PEN is shown in Figure 10. The dielectric constant of GS-Zn-CNT/PEN is as high as 78.0 at 100 Hz, with an increment of 2000% in comparison with PEN, even the content of GO-Zn-CNT is just 2.0 wt%. Besides, the loss tangent of GS-Zn-CNT/PEN

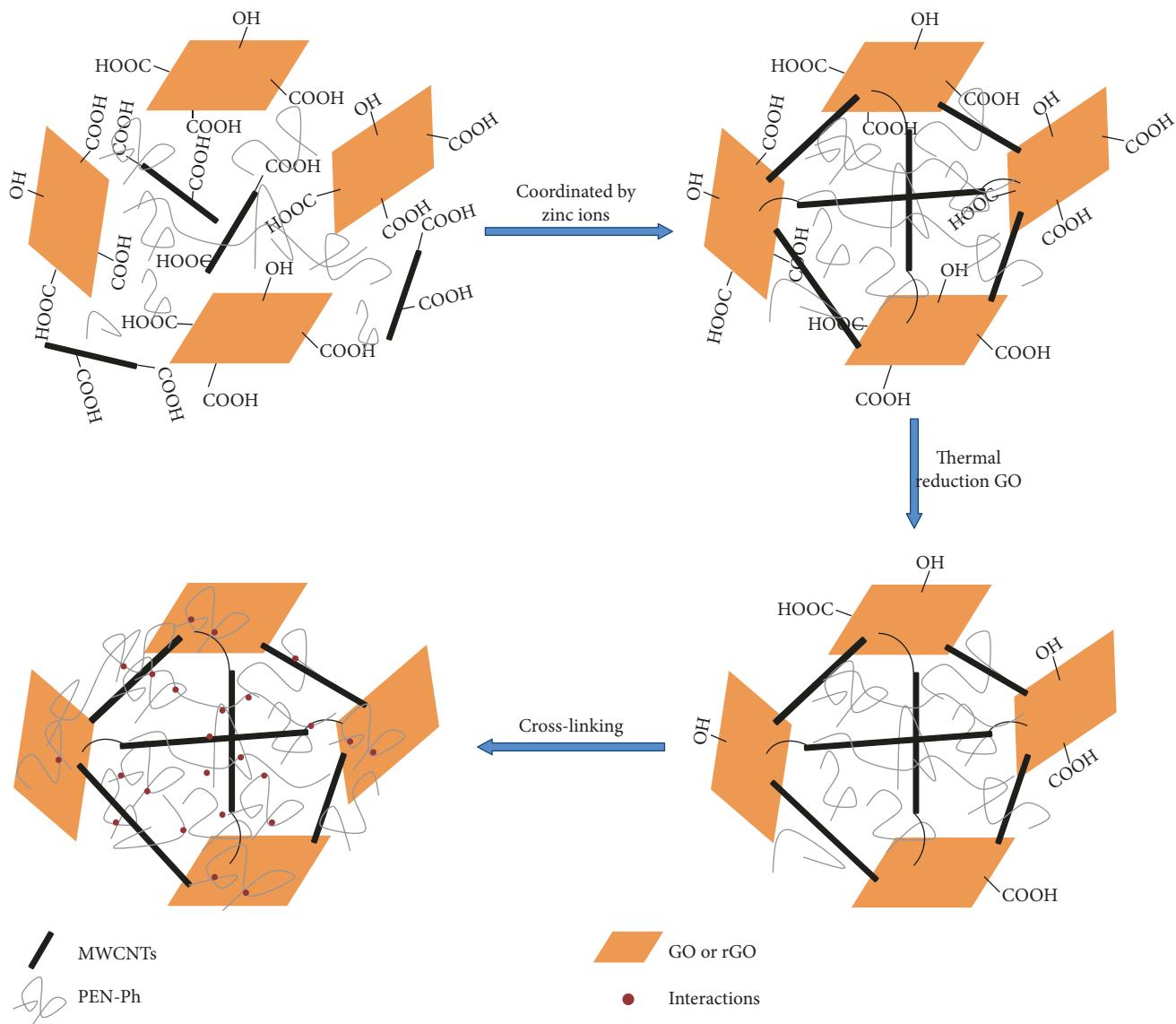


FIGURE 10: Fabrication route for GS-Zn-CNT/CPEN.

is 0.18 at 100 Hz when the content of GO-Zn-CNT is 2.0 wt%, but it is much lower compared with that of graphene/PEN nanocomposites (0.82 at 100 Hz with 2.0 wt% graphene). Therefore, it is also an effective method to prepare graphene-based high- k composite materials.

4. Conclusions

In conclusion, high- k dielectrics for high-energy storage need to possess high permittivity, low dielectric loss, and excellent mechanical strength as well as high thermal stability. Up to now, there is not any single-component dielectric meeting the mentioned requirement for high-temperature applications. The composting of thermal stable PEN with high dielectric constant additives (such as organic fillers, ceramic fillers, and conductive fillers) is an efficacious technique for the development of thermal resisting high- k dielectrics. Although some important progresses have been made in

the research of PEN-based composite dielectric materials in recent years, it still cannot fully meet the development of the electronic industry. This research news article mainly reviews the progress of PEN-based composites for electronic applications. It preliminarily revealed the effects of polymer substrate, type of filler, surface modification, and preparation procedure on PEN composites' dielectric properties. To sum up, the PEN incorporated with organic fillers exhibits relative high permittivity, low loss tangent, excellent mechanical strength, and thermal stability, but the improvement of permittivity is inadequate because of the limited permittivity of these organic fillers. Ferroelectric ceramics can effectively enhance permittivity of PEN-based nanocomposites. However, a high loading fraction is usually needed, which reduces the mechanical performances of the system simultaneously. In comparison, dielectric constant of PEN composites filled with conductive fillers could be significantly increased at lower filling fraction. However, the conductivity of the

composites was also improved, which leads to the corresponding high dielectric loss. As a result, the research and preparation of high- k dielectric materials still face many challenges, which are the goal of future efforts. Further research can be carried out in the following aspects: firstly, preparing the new additives with controllable structure, morphology, size, and so on and exploring some new and simple compositing technology and interface control technology and secondly, researching and developing dielectric composite materials with stable performance in special environments such as high temperature and frequency. Thirdly, fabricating high- k composites exhibits high permittivity, low-loss tangent, and other required performances simultaneously with controllable procedures.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Authors' Contributions

Yong You and Chenhao Zhan contributed equally to this work.

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References

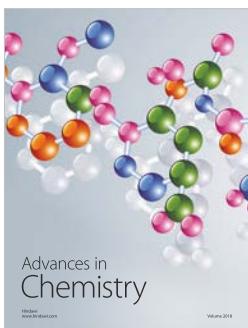
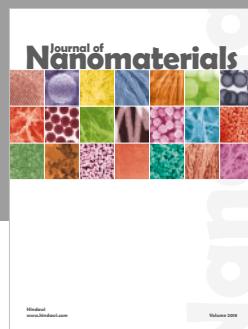
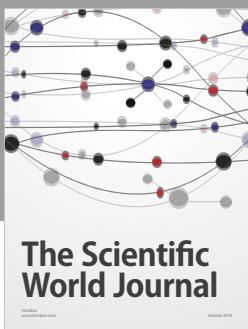
- [1] J. K. Yuan, S. H. Yao, Z. M. Dang, A. Sylvestre, M. Genestoux, and J. Bai, "Giant dielectric permittivity nanocomposites: realizing true potential of pristine carbon nanotubes in polyvinylidene fluoride matrix through an enhanced interfacial interaction," *The Journal of Physical Chemistry C*, vol. 115, no. 13, pp. 5515–5521, 2011.
- [2] L. Qi, B. I. Lee, S. Chen, W. D. Samuels, and G. J. Exarhos, "High-dielectric-constant silver-epoxy composites as embedded dielectrics," *Advanced Materials*, vol. 17, no. 14, pp. 1777–1781, 2005.
- [3] T. Kousksou, P. Bruel, A. Jamil, T. el Rhafiki, and Y. Zeraouli, "Energy storage: applications and challenges," *Solar Energy Materials and Solar Cells*, vol. 120, pp. 59–80, 2014.
- [4] R. M. Dell and D. A. J. Rand, "Energy storage — a key technology for global energy sustainability," *Journal of Power Sources*, vol. 100, no. 1-2, pp. 2–17, 2001.
- [5] Y. Wang and Y. Xia, "Recent progress in supercapacitors: from materials design to system construction," *Advanced Materials*, vol. 25, no. 37, pp. 5336–5342, 2013.
- [6] Z. M. Dang, L. Wang, Y. Yin, Q. Zhang, and Q. Q. Lei, "Giant dielectric permittivities in functionalized carbon-nanotube/electroactive-polymer nanocomposites," *Advanced Materials*, vol. 19, no. 6, pp. 852–857, 2007.
- [7] W. H. Xu, G. Yang, L. Jin et al., "High- k polymer nanocomposites filled with hyperbranched phthalocyanine-coated BaTiO₃ for high-temperature and elevated field applications," *ACS Applied Materials & Interfaces*, vol. 10, no. 13, pp. 11233–11241, 2018.
- [8] M. A. Alam, M. H. Azarian, and M. G. Pecht, "Effects of moisture absorption on the electrical parameters of embedded capacitors with epoxy-BaTiO₃ nanocomposite dielectric," *Journal of Materials Science: Materials in Electronics*, vol. 23, no. 8, pp. 1504–1510, 2012.
- [9] A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. van Schalkwijk, "Nanostructured materials for advanced energy conversion and storage devices," *Nature Materials*, vol. 4, no. 5, pp. 366–377, 2005.
- [10] J. Xu and C. P. Wong, "Characterization and properties of an organic-inorganic dielectric nanocomposite for embedded decoupling capacitor applications," *Composites Part A: Applied Science and Manufacturing*, vol. 38, no. 1, pp. 13–19, 2007.
- [11] Y. Rao and C. P. Wong, "Material characterization of a high-dielectric-constant polymer-ceramic composite for embedded capacitor for RF applications," *Journal of Applied Polymer Science*, vol. 92, no. 4, pp. 2228–2231, 2004.
- [12] M. Rahimabady, M. S. Mirshekarloo, K. Yao, and L. Lu, "Dielectric behaviors and high energy storage density of nanocomposites with core-shell BaTiO₃@TiO₂ in poly(vinylidene fluoride-hexafluoropropylene)," *Physical Chemistry Chemical Physics*, vol. 15, no. 38, pp. 16242–16248, 2013.
- [13] J. Xu and C. P. Wong, "Low-loss percolative dielectric composite," *Applied Physics Letters*, vol. 87, no. 8, article 082907, 2005.
- [14] Z. M. Dang, Y. J. Xia, J. W. Zha, J. K. Yuan, and J. Bai, "Preparation and dielectric properties of surface modified TiO₂/silicone rubber nanocomposites," *Materials Letters*, vol. 65, no. 23-24, pp. 3430–3432, 2011.
- [15] H. Zheng, J. Wang, S. E. Lofland et al., "Multiferroic BaTiO₃-CoFe₂O₄ nanostructures," *Science*, vol. 303, no. 5658, pp. 661–663, 2004.
- [16] Y. Gao, M. Yuan, X. Sun, and J. Ouyang, "In situ preparation of high quality BaTiO₃ dielectric films on Si at 350–500°C," *Journal of Materials Science: Materials in Electronics*, vol. 28, no. 1, pp. 337–343, 2017.
- [17] G. Arlt, D. Hennings, and G. de With, "Dielectric properties of fine-grained barium titanate ceramics," *Journal of Applied Physics*, vol. 58, no. 4, pp. 1619–1625, 1985.
- [18] K. L. Choi, N. Na, and M. Swaminathan, "Characterization of embedded passives using macromodels in LTCC technology," *IEEE Transactions on Components, Packaging, and Manufacturing Technology: Part B*, vol. 21, no. 3, pp. 258–268, 1998.
- [19] M. A. Ramírez, P. R. Bueno, R. Tararam, A. A. Cavalheiro, E. Longo, and J. A. Varela, "Evaluation of the effect of the stoichiometric ratio of Ca/Cu on the electrical and microstructural properties of the CaCu₃Ti₄O₁₂ polycrystalline system," *Journal of Physics D: Applied Physics*, vol. 42, no. 18, pp. 185503–185510, 2009.
- [20] A. Eigner and S. Semino, "50 years of electrical-stress control in cable accessories," *IEEE Electrical Insulation Magazine*, vol. 29, no. 5, pp. 47–55, 2013.
- [21] H. Wang, W. Zhong, P. Xu, and Q. Du, "Properties of polyimide/silica nanohybrids from silicic acid oligomer," *Macromolecular Materials and Engineering*, vol. 289, no. 9, pp. 793–799, 2004.
- [22] J. Jumpatam, P. Thongbai, B. Kongsook, T. Yamwong, and S. Maensiri, "High permittivity, low dielectric loss, and high

- electrostatic potential barrier in $\text{Ca}_2\text{Cu}_2\text{Ti}_4\text{O}_{12}$ ceramics," *Materials Letters*, vol. 76, no. 1, pp. 40–42, 2012.
- [23] B. Chu, X. Zhou, K. Ren et al., "A dielectric polymer with high electric energy density and fast discharge speed," *Science*, vol. 313, no. 5785, pp. 334–336, 2006.
- [24] K. Yu, Y. Niu, Y. Zhou, Y. Bai, and H. Wang, "Nanocomposites of surface-modified BaTiO_3 nanoparticles filled ferroelectric polymer with enhanced energy density," *Journal of the American Ceramic Society*, vol. 96, no. 8, pp. 2519–2524, 2013.
- [25] Q. Li, G. Zhang, X. Zhang, S. Jiang, Y. Zeng, and Q. Wang, "Relaxor ferroelectric-based electrocaloric polymer nanocomposites with a broad operating temperature range and high cooling energy," *Advanced Materials*, vol. 27, no. 13, pp. 2236–2241, 2015.
- [26] L. Zhu and Q. Wang, "Novel ferroelectric polymers for high energy density and low loss dielectrics," *Macromolecules*, vol. 45, no. 7, pp. 2937–2954, 2012.
- [27] X. H. Tang, Y. You, H. Mao, K. Li, R. B. Wei, and X. B. Liu, "Energy storage of polyarylene ether nitriles at high temperature," *Electronic Materials Letters*, vol. 14, no. 4, pp. 440–445, 2018.
- [28] J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, "Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites," *Carbon*, vol. 44, no. 9, pp. 1624–1652, 2006.
- [29] S. K. Hwang, I. Bae, S. M. Cho, R. H. Kim, H. J. Jung, and C. Park, "High performance multi-level non-volatile polymer memory with solution-blended ferroelectric polymer/high-k insulators for low voltage operation," *Advanced Functional Materials*, vol. 23, no. 44, pp. 5484–5493, 2013.
- [30] M. Kaseem, K. Hamad, and Y. G. Ko, "Fabrication and materials properties of polystyrene/carbon nanotube (PS/CNT) composites: a review," *European Polymer Journal*, vol. 79, pp. 36–62, 2016.
- [31] R. Ma, A. F. Baldwin, C. Wang et al., "Rationally designed polyimides for high-energy density capacitor applications," *ACS Applied Materials & Interfaces*, vol. 6, no. 13, pp. 10445–10451, 2014.
- [32] L. Zhang, S. Chen, S. Yuan, D. Wang, P. H. Hu, and Z. M. Dang, "Low dielectric loss and weak frequency dependence of dielectric permittivity of the $\text{CeO}_2/\text{polystyrene}$ nanocomposite films," *Applied Physics Letters*, vol. 105, no. 5, article 052905, 2014.
- [33] B. Luo, X. Wang, Y. Wang, and L. Li, "Fabrication, characterization, properties and theoretical analysis of ceramic/PVDF composite flexible films with high dielectric constant and low dielectric loss," *Journal of Materials Chemistry A*, vol. 2, no. 2, pp. 510–519, 2014.
- [34] H. Li, Z. Li, F. Lin, Y. Chen, D. Liu, and B. Wang, "Insulation resistance of metallized polypropylene film capacitors under different electric fields," *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 20, no. 4, pp. 1315–1320, 2013.
- [35] R. Yang, R. Wei, K. Li, L. Tong, K. Jia, and X. Liu, "Cross-linked polyarylene ether nitrile film as flexible dielectric materials with ultrahigh thermal stability," *Scientific Reports*, vol. 6, no. 1, article 36434, 2016.
- [36] F. Meng, R. Zhao, Y. Zhan, and X. Liu, "Design of thorn-like micro/nanofibers: fabrication and controlled morphology for engineered composite materials applications," *Journal of Materials Chemistry*, vol. 21, no. 41, pp. 16385–16390, 2011.
- [37] J. Yang, H. Tang, Y. Zhan, H. Guo, R. Zhao, and X. Liu, "Photoelectric properties of poly(arylene ether nitriles)-copper phthalocyanine conjugates complex via in situ polymerization," *Materials Letters*, vol. 72, pp. 42–45, 2012.
- [38] X. Huang, M. Feng, and X. Liu, "Design of bristle-like TiO_2 -MWCNT nanotubes to improve the dielectric and interfacial properties of polymer-based composite films," *RSC Advances*, vol. 4, no. 10, pp. 4985–4992, 2014.
- [39] H. Mao, Y. You, L. F. Tong, X. H. Tang, R. B. Wei, and X. B. Liu, "Dielectric properties of diblock copolymers containing a polyarylene ether nitrile block and a polyarylene ether ketone block," *Journal of Materials Science: Materials in Electronics*, vol. 29, no. 4, pp. 3127–3134, 2017.
- [40] L. Tong, R. Wei, J. Wang, and X. Liu, "Phthalonitrile end-capped polyarylene ether nitrile nanocomposites with Cu^{2+} bridged carbon nanotube and graphene oxide network," *Materials Letters*, vol. 178, pp. 312–315, 2016.
- [41] K. Abe, D. Nagao, and M. Konno, "Fabrication of highly refractive BaTiO_3 nanocomposite films using heat resistant polymer as matrix," *European Polymer Journal*, vol. 49, no. 11, pp. 3455–3459, 2013.
- [42] M. Xu, T. Zhang, B. Gu, J. Wu, and Q. Chen, "Synthesis and properties of novel polyurethane–urea/multiwalled carbon nanotube composites," *Macromolecules*, vol. 39, no. 10, pp. 3540–3545, 2006.
- [43] L. Xie, X. Huang, Y. Huang, K. Yang, and P. Jiang, "Core-shell structured hyperbranched aromatic polyamide/ BaTiO_3 hybrid filler for poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) nanocomposites with the dielectric constant comparable to that of percolative composites," *ACS Applied Materials & Interfaces*, vol. 5, no. 5, pp. 1747–1756, 2013.
- [44] S. A. Paniagua, Y. Kim, K. Henry, R. Kumar, J. W. Perry, and S. R. Marder, "Surface-initiated polymerization from barium titanate nanoparticles for hybrid dielectric capacitors," *ACS Applied Materials & Interfaces*, vol. 6, no. 5, pp. 3477–3482, 2014.
- [45] L. Xie, X. Huang, C. Wu, and P. Jiang, "Core-shell structured poly(methyl methacrylate)/ BaTiO_3 nanocomposites prepared by in situ atom transfer radical polymerization: a route to high dielectric constant materials with the inherent low loss of the base polymer," *Journal of Materials Chemistry*, vol. 21, no. 16, pp. 5897–5906, 2011.
- [46] B. Balasubramanian, K. L. Kraemer, N. A. Reding, R. Skomski, S. Ducharme, and D. J. Sellmyer, "Synthesis of monodisperse TiO_2 -paraffin core-shell nanoparticles for improved dielectric properties," *ACS Nano*, vol. 4, no. 4, pp. 1893–1900, 2010.
- [47] Z. Li, L. A. Fredin, P. Tewari et al., "In situ catalytic encapsulation of core-shell nanoparticles having variable shell thickness: dielectric and energy storage properties of high-permittivity metal oxide nanocomposites," *Chemistry of Materials*, vol. 22, no. 18, pp. 5154–5164, 2010.
- [48] X. Pang, Y. He, B. Jiang et al., "Block copolymer/ferroelectric nanoparticle nanocomposites," *Nanoscale*, vol. 5, no. 18, pp. 8695–8702, 2013.
- [49] Y. U. Wang and D. Q. Tan, "Computational study of filler microstructure and effective property relations in dielectric composites," *Journal of Applied Physics*, vol. 109, no. 10, pp. 104102–104109, 2011.
- [50] S. Ducharme, "An inside-out approach to storing electrostatic energy," *ACS Nano*, vol. 3, no. 9, pp. 2447–2450, 2009.

- [51] A. Maliakal, H. Katz, P. M. Cotts, S. Subramoney, and P. Mirau, "Inorganic oxide core, polymer shell nanocomposite as a high K gate dielectric for flexible electronics applications," *Journal of the American Chemical Society*, vol. 127, no. 42, pp. 14655–14662, 2005.
- [52] A. Kahouli, O. Gallot-Lavallée, P. Rain et al., "Structure effect of thin film polypropylene view by dielectric spectroscopy and X-ray diffraction: application to dry type power capacitors," *Journal of Applied Polymer Science*, vol. 132, no. 39, 2015.
- [53] M. Sharma, M. P. Singh, C. Srivastava, G. Madras, and S. Bose, "Poly(vinylidene fluoride)-based flexible and lightweight materials for attenuating microwave radiations," *ACS Applied Materials & Interfaces*, vol. 6, no. 23, pp. 21151–21160, 2014.
- [54] Y. You, X. Huang, Z. Pu, K. Jia, and X. Liu, "Enhanced crystallinity, mechanical and dielectric properties of biphenyl polyarylene ether nitriles by unidirectional hot-stretching," *Journal of Polymer Research*, vol. 22, no. 11, 2015.
- [55] X. Liu, S. Long, D. Luo, W. Chen, and G. Cao, "Preparation and properties of polyarylene ether nitrile/multi-walled carbon nanotubes composites," *Materials Letters*, vol. 62, no. 1, pp. 19–22, 2008.
- [56] Y. You, X. Du, H. Mao, X. Tang, R. Wei, and X. Liu, "Synergistic enhancement of mechanical, crystalline and dielectric properties of polyarylene ether nitrile-based nanocomposites by unidirectional hot stretching-quenching," *Polymer International*, vol. 66, no. 8, pp. 1151–1158, 2017.
- [57] L. Tong, K. Jia, and X. Liu, "Novel phthalonitrile-terminated polyarylene ether nitrile with high glass transition temperature and enhanced thermal stability," *Materials Letters*, vol. 128, pp. 267–270, 2014.
- [58] H. Tang, J. Yang, J. Zhong, R. Zhao, and X. Liu, "Synthesis of high glass transition temperature fluorescent polyarylene ether nitrile copolymers," *Materials Letters*, vol. 65, no. 11, pp. 1703–1706, 2011.
- [59] Y. Zhan, F. Meng, X. Yang, Y. Lei, R. Zhao, and X. Liu, "Synthesis, characterization and properties of multifunctional poly(arylene ether nitriles) (PEN)/CNTs/Fe₃O₄ nanocomposites," *Journal of Polymer Science Part B: Polymer Physics*, vol. 49, no. 8, pp. 611–619, 2011.
- [60] X. B. Liu, R. H. Du, L. L. Hao, S. Wang, G. P. Cao, and H. Jiang, "Synthesis, characterization and rheological property of biphenyl-based polyarylene ether nitrile copolymers," *Express Polymer Letters*, vol. 1, no. 8, pp. 499–505, 2007.
- [61] Z. Pu, H. Tang, X. Huang et al., "Effect of surface functionalization of SiO₂ particles on the interfacial and mechanical properties of PEN composite films," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 415, pp. 125–133, 2012.
- [62] L. Xie, X. Huang, K. Yang, S. Li, and P. Jiang, "Grafting to route to PVDF-HFP-GMA/BaTiO₃ nanocomposites with high dielectric constant and high thermal conductivity for energy storage and thermal management applications," *Journal of Materials Chemistry A*, vol. 2, no. 15, pp. 5244–5251, 2014.
- [63] J. W. Wang, Q. D. Shen, C. Z. Yang, and Q. M. Zhang, "High dielectric constant composite of P(VDF-TrFE) with grafted copper phthalocyanine oligomer," *Macromolecules*, vol. 37, no. 6, pp. 2294–2298, 2004.
- [64] Q. M. Zhang, H. Li, M. Poh et al., "An all-organic composite actuator material with a high dielectric constant," *Nature*, vol. 419, no. 6904, pp. 284–287, 2002.
- [65] Z. Pu, R. Wei, and X. Liu, "Influence of unidirectional hot-stretching on the mechanical and dielectric properties of polymer-based composites," in *Energy Science and Applied Technology ESAT 2016: Proceedings of the International Conference on Energy Science and Applied Technology (ESAT 2016)*, pp. 191–194, Wuhan, China, 2016.
- [66] K. Jia, L. Pan, Z. Wang et al., "Morphology and photophysical properties of dual-emissive hyperbranched zinc phthalocyanines and their self-assembling superstructures," *Journal of Materials Science*, vol. 51, no. 6, pp. 3191–3199, 2016.
- [67] R. Yang, K. Li, L. Tong, K. Jia, and X. Liu, "The relationship between processing and performances of polyarylene ether nitriles terminated with phthalonitrile/trifunctional phthalonitrile composites," *Journal of Polymer Research*, vol. 22, no. 11, p. 210, 2015.
- [68] Y. Huang, Y. Luo, M. Xu, Y. Lei, and X. Liu, "Studied on mechanical, thermal and dielectric properties of BPh/PEN-OH copolymer," *Composites Part B: Engineering*, vol. 106, no. 1, pp. 294–299, 2016.
- [69] C. Long, R. Wei, X. Huang, M. Feng, K. Jia, and X. Liu, "Mechanical, dielectric, and rheological properties of poly(arylene ether nitrile)-reinforced poly(vinylidene fluoride)," *High Performance Polymers*, vol. 29, no. 2, pp. 178–186, 2017.
- [70] R. Wei, K. Li, J. Ma, H. Zhang, and X. Liu, "Improving dielectric properties of polyarylene ether nitrile with conducting polyaniline," *Journal of Materials Science: Materials in Electronics*, vol. 27, no. 9, pp. 9565–9571, 2016.
- [71] V. S. Nisa, S. Rajesh, K. P. Murali, V. Priyadarsini, S. N. Potty, and R. Ratheesh, "Preparation, characterization and dielectric properties of temperature stable SrTiO₃/PEEK composites for microwave substrate applications," *Composites Science and Technology*, vol. 68, no. 1, pp. 106–112, 2008.
- [72] Y. Hu, Y. Zhang, H. Liu, and D. Zhou, "Microwave dielectric properties of PTFE/CaTiO₃ polymer ceramic composites," *Ceramics International*, vol. 37, no. 5, pp. 1609–1613, 2011.
- [73] D. Padalia, G. Bisht, U. C. Johri, and K. Asokan, "Fabrication and characterization of cerium doped barium titanate/PMMA nano-composites," *Solid State Sciences*, vol. 19, no. 5, pp. 122–129, 2013.
- [74] T. Hoshina, "Size effect of barium titanate fine particles and ceramics," *Journal of the Ceramic Society of Japan*, vol. 121, no. 1410, pp. 156–161, 2013.
- [75] H. Tang, J. Zhong, J. Yang, Z. Ma, and X. Liu, "Flexible polyarylene ether nitrile/BaTiO₃ nanocomposites with high energy density for film capacitor applications," *Journal of Electronic Materials*, vol. 40, no. 2, pp. 141–148, 2011.
- [76] B. Schumacher, H. Geßwein, J. Haußelt, and T. Hanemann, "Temperature treatment of nano-scaled barium titanate filler to improve the dielectric properties of high-k polymer based composites," *Microelectronic Engineering*, vol. 87, no. 10, pp. 1978–1983, 2010.
- [77] Y. Sun, Z. Zhang, and C. P. Wong, "Influence of interphase and moisture on the dielectric spectroscopy of epoxy/silica composites," *Polymer*, vol. 46, no. 7, pp. 2297–2305, 2005.
- [78] Y. Kobayashi, T. Tanase, T. Tabata, T. Miwa, and M. Konno, "Fabrication and dielectric properties of the BaTiO₃-polymer nano-composite thin films," *Journal of the European Ceramic Society*, vol. 28, no. 1, pp. 117–122, 2008.
- [79] P. Kim, S. C. Jones, P. J. Hotchkiss et al., "Phosphonic acid-modified barium titanate polymer nanocomposites with high

- permittivity and dielectric strength," *Advanced Materials*, vol. 19, no. 7, pp. 1001–1005, 2007.
- [80] Y. Rao, A. Takahashi, and C. P. Wong, "Di-block copolymer surfactant study to optimize filler dispersion in high dielectric constant polymer-ceramic composite," *Composites Part A: Applied Science and Manufacturing*, vol. 34, no. 11, pp. 1113–1116, 2003.
- [81] S. J. Chang, W. S. Liao, C. J. Ciou, J. T. Lee, and C. C. Li, "An efficient approach to derive hydroxyl groups on the surface of barium titanate nanoparticles to improve its chemical modification ability," *Journal of Colloid and Interface Science*, vol. 329, no. 2, pp. 300–305, 2009.
- [82] H. Tang, P. Wang, P. Zheng, and X. Liu, "Core-shell structured BaTiO₃@polymer hybrid nanofiller for poly(arylene ether nitrile) nanocomposites with enhanced dielectric properties and high thermal stability," *Composites Science and Technology*, vol. 123, pp. 134–142, 2016.
- [83] X. Huang, Z. Pu, L. Tong, Z. Wang, and X. Liu, "Preparation and dielectric properties of surface modified TiO₂/PEN composite films with high thermal stability and flexibility," *Journal of Materials Science: Materials in Electronics*, vol. 23, no. 12, pp. 2089–2097, 2012.
- [84] H. Tang, Z. Ma, J. Zhong, J. Yang, R. Zhao, and X. Liu, "Effect of surface modification on the dielectric properties of PEN nanocomposites based on double-layer core/shell-structured BaTiO₃ nanoparticles," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 384, no. 1–3, pp. 311–317, 2011.
- [85] Y. You, W. Han, L. Tu, Y. Wang, R. Wei, and X. Liu, "Double-layer core/shell-structured nanoparticles in polyarylene ether nitrile-based nanocomposites as flexible dielectric materials," *RSC Advances*, vol. 7, no. 47, pp. 29306–29311, 2017.
- [86] F. He, S. Lau, H. L. Chan, and J. Fan, "High dielectric permittivity and low percolation threshold in nanocomposites based on poly(vinylidene fluoride) and exfoliated graphite nanoplates," *Advanced Materials*, vol. 21, no. 6, pp. 710–715, 2009.
- [87] K. Li, L. Tong, R. Yang, R. Wei, and X. Liu, "In-situ preparation and dielectric properties of silver-polyarylene ether nitrile nanocomposite films," *Journal of Materials Science: Materials in Electronics*, vol. 27, no. 5, pp. 4559–4565, 2016.
- [88] Y. You, R. Wei, R. Yang, W. Yang, X. Hua, and X. Liu, "Crystallization behaviors of polyarylene ether nitrile filled in multi-walled carbon nanotubes," *RSC Advances*, vol. 6, no. 75, pp. 70877–70883, 2016.
- [89] A. R. Kamali, H. K. Kim, K. B. Kim, R. Vasant Kumar, and D. J. Fray, "Large scale green production of ultra-high capacity anode consisting of graphene encapsulated silicon nanoparticles," *Journal of Materials Chemistry A*, vol. 5, no. 36, pp. 19126–19135, 2017.
- [90] Y. Shen, Y. Lin, M. Li, and C.-W. Nan, "High dielectric performance of polymer composite films induced by a percolating interparticle barrier layer," *Advanced Materials*, vol. 19, no. 10, pp. 1418–1422, 2007.
- [91] T. S. Kelby, M. Wang, and W. T. S. Huck, "Controlled folding of 2D Au–polymer brush composites into 3D microstructures," *Advanced Functional Materials*, vol. 21, no. 4, pp. 652–657, 2011.
- [92] Z. Pu, L. Tong, M. Feng, K. Jia, and X. Liu, "Influence of hyperbranched copper phthalocyanine grafted carbon nanotubes on the dielectric and rheological properties of polyarylene ether nitriles," *RSC Advances*, vol. 5, no. 88, pp. 72028–72036, 2015.
- [93] M. Ruan, J. Guan, D. He, T. Meng, and Q. Zhang, "The hydrogenation of aromatic-naphthalene with Ni₂P/CNTs," *RSC Advances*, vol. 5, no. 71, pp. 57700–57703, 2015.
- [94] P. Zheng, Z. Pu, W. Yang, S. Shen, K. Jia, and X. Liu, "Effect of multiwalled carbon nanotubes on the crystallization and dielectric properties of BP-PEN nanocomposites," *Journal of Materials Science: Materials in Electronics*, vol. 25, no. 9, pp. 3833–3839, 2014.
- [95] H. H. So, J. W. Cho, and N. G. Sahoo, "Effect of carbon nanotubes on mechanical and electrical properties of polyimide/carbon nanotubes nanocomposites," *European Polymer Journal*, vol. 43, no. 9, pp. 3750–3756, 2007.
- [96] F. Jin, M. Feng, K. Jia, and X. Liu, "Aminophenoxyphthalonitrile modified MWCNTs/polyarylene ether nitriles composite films with excellent mechanical, thermal, dielectric properties," *Journal of Materials Science: Materials in Electronics*, vol. 26, no. 7, pp. 5152–5160, 2015.
- [97] Z. Pu, X. Huang, L. Chen, J. Yang, H. Tang, and X. Liu, "Effect of nitrile-functionalization and thermal cross-linking on the dielectric and mechanical properties of PEN/CNTs-CN composites," *Journal of Materials Science: Materials in Electronics*, vol. 24, no. 8, pp. 2913–2922, 2013.
- [98] X. Huang, M. Feng, and X. Liu, "Synergistic enhancement of dielectric constant of novel core/shell BaTiO₃@MWCNTs/PEN nanocomposites with high thermal stability," *Journal of Materials Science: Materials in Electronics*, vol. 25, no. 1, pp. 97–102, 2014.
- [99] X. Huang, K. Wang, K. Jia, and X. Liu, "Preparation of TiO₂-MWCNT core/shell heterostructures containing a single MWCNT and their electromagnetic properties," *Composite Interfaces*, vol. 22, no. 5, pp. 343–351, 2015.
- [100] Q. Xiao, R. Yang, Y. You, H. Zhang, R. Wei, and X. Liu, "Crystalline, mechanical and dielectric properties of polyarylene ether nitrile with multi-walled carbon nanotube filled with polyarylene ether nitrile," *Journal of Nanoscience and Nanotechnology*, vol. 18, no. 6, pp. 4311–4317, 2018.
- [101] A. G. Garcia, S. E. Baltazar, A. H. R. Castro, J. F. P. Robles, and A. Rubio, "Influence of S and P doping in a graphene sheet," *Journal of Computational and Theoretical Nanoscience*, vol. 5, no. 11, pp. 2221–2229, 2008.
- [102] Z. Wang, W. Yang, and X. Liu, "Electrical properties of poly(arylene ether nitrile)/graphene nanocomposites prepared by in situ thermal reduction route," *Journal of Polymer Research*, vol. 21, no. 2, p. 358, 2014.
- [103] M. Fang, K. Wang, H. Lu, Y. Yang, and S. Nutt, "Single-layer graphene nanosheets with controlled grafting of polymer chains," *Journal of Materials Chemistry*, vol. 20, no. 10, pp. 1982–1992, 2010.
- [104] J. Yang, M. Wu, F. Chen, Z. Fei, and M. Zhong, "Preparation, characterization, and supercritical carbon dioxide foaming of polystyrene/graphene oxide composites," *Journal of Supercritical Fluids*, vol. 56, no. 2, pp. 201–207, 2011.
- [105] A. L. Higginbotham, J. R. Lomeda, A. B. Morgan, and J. M. Tour, "Graphite oxide flame-retardant polymer nanocomposites," *ACS Applied Materials & Interfaces*, vol. 1, no. 10, pp. 2256–2261, 2009.
- [106] W. S. Hummers Jr. and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the American Chemical Society*, vol. 80, no. 6, pp. 1339–1339, 1958.

- [107] Z. Ma, D. Liu, Y. Zhu et al., "Graphene oxide/chitin nanofibril composite foams as column adsorbents for aqueous pollutants," *Carbohydrate Polymers*, vol. 144, no. 25, pp. 230–237, 2016.
- [108] J. Li, Z. Pu, Z. Wang, Y. Long, K. Jia, and X. Liu, "High dielectric constants of composites of fiber-like copper phthalocyanine-coated graphene oxide embedded in poly(-arylene ether nitriles)," *Journal of Electronic Materials*, vol. 44, no. 7, pp. 2378–2386, 2015.
- [109] Y. Zhan, X. Yang, H. Guo, J. Yang, F. Meng, and X. Liu, "Cross-linkable nitrile functionalized graphene oxide/poly(-arylene ether nitrile) nanocomposite films with high mechanical strength and thermal stability," *Journal of Materials Chemistry*, vol. 22, no. 12, pp. 5602–5608, 2012.
- [110] J. Wang, R. Wei, L. Tong, and X. Liu, "Effect of magnetite bridged carbon nanotube/graphene networks on the properties of polyarylene ether nitrile," *Journal of Materials Science: Materials in Electronics*, vol. 28, no. 5, pp. 3978–3986, 2017.
- [111] R. Wei, J. Wang, H. Zhang, W. Han, and X. Liu, "Crosslinked polyarylene ether nitrile interpenetrating with zinc ion bridged graphene sheet and carbon nanotube network," *Polymer*, vol. 9, no. 12, p. 342, 2017.





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