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High-*k* Polymer Nanocomposites for Energy Storage Applications

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Abstract

High dielectric (high-k) polymer nanocomposites that can electrostatically store energy are widely used in electronics and electric power systems due to their high breakdown strengths (E_b), durability, and ability to configure in various shapes. However, these nanocomposites suffer from a limited working temperature regime, thus limiting their extreme applications, such as hybrid and electric vehicles, aerospace power electronics, and deep ground fuel exploration. Furthermore, the E_b and the electric displacement (D) of polymer nanocomposites must be simultaneously enhanced for high-density capacitor applications, which prove to be difficult to modify concurrently. This chapter thoroughly reviews (investigates) the recent developments in the high-k polymer nanocomposites synthesis, characterization, and energy storage applications. Consequently, the aim of this chapter is to provide an overview of the novel developmental strategies in order to develop high-dielectric nanocomposites perovskite ceramics that can be incorporated in high-energy-density (HED) applications.

Keywords: polymer nanocomposites, capacitors, perovskite ceramics, dielectric constant, energy density applications

1. Introduction

Highdielectric constant (*high-k*) materials and polymer nanocomposites are under extensive investigation because of their potential applications in organic field-effect transistors (OFETs), invertors, electro-optics, energy, humidity and temperature sensor applications. The magnitude of *k* for silicon dioxide (SiO₂) is given as 3.9. Materials that exhibit k > 3.9 are classified as



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. [cc) BY high-*k*, and materials whose k < 3.9 are classified as low-*k* materials. Polymer dielectric nanocomposites are generally composed of dielectric polymers as the matrix material, and inorganic/organic fillers as the reinforcement, utilizing the properties of both. Polymers have been found to demonstrate high breakdown strengths along with high energy density (HED), while the fillers, especially dielectric ceramics, have a high dielectric constant (*k*). The combination of both provides superior dielectric properties depending on the type and nature of the polymer matrices as well as the fillers. The total energy storage density (U) of a capacitor is given as Eq. (1).

$$U = \int E dD$$
(1)

where **E** and D are the applied electric field and electric displacement, respectively. The magnitude of U for the linear dielectrics is defined as Eq. (2).

$$\mathbf{U} = 1/2\mathbf{D}\mathbf{E} + 1/2k\varepsilon_0\mathbf{E}^2$$
⁽²⁾

Where, *k* is the dielectric constant and $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of free space. Therefore, the magnitude of U in Eq. (2) depends on the values of both *k* and E. However, limitations exist in ceramic and electrolytic capacitors, such as the applied E of a material is restricted to the breakdown strength of the same material. Due to these deficiencies, polymer capacitors have proven to be better alternatives for high energy density applications because of their high E_{br} easy and economical processing, and flexibility in designing [1–3].

For high energy density applications, various ceramic fillers have been reported in the recent literature, such as barium titanate (BaTiO₃, BT), barium strontium titanate $(Ba_{1-r}Sr_{r}TiO_{3})$, barium zirconate titanate $(BaZr_{r}Ti_{1-r}O_{3})$, lead zirconate titanate $(PbZr_{r}Ti_{1-r}O_{3})$, metal phenylphosphonates $ATi(O_3PC_6H_5)_3$, where A = Mg, Ca, Sr, Ba, Pb, MnCoFe₂O₄, and MnCuFe₂O₄ [4–6]. The inorganic-organic nanocomposites have been processed by various techniques. Generally, the presynthesized filler nanoparticles are dispersed in the polymer matrix. Another method known as the in situ sol-gel involves the hydrothermal treatment of the filler precursor/polymer system in hydroxide solution. The filler particles are synthesized at the precursor sites in the polymeric system. Despite several modifications in these synthetic procedures, the final materials still exhibit conglomeration, which is responsible for the inconsistent behavior of the system. Furthermore, due to the incompatibility of the polymer-precursor and possible gel formation overtime, the system properties are compromised [7]. Zhu et al. [8] investigated the core-shell structured polymer@BT nanoparticles by using a polymer shells with different elemental properties in order to study the effect of core-shell in detail for surface modifications. A surface-initiated reversible-addition-fragmentation chain transfer (RAFT) polymerization method was used, where the thicknesses of the polymer shells were maintained to the same values. Results of this study indicated that for high energy density applications, high dielectric constant and low electrical conductivity are required. The importance of conductivity of the shell material in the final device performance was also reported in this investigation [8]. Other filler materials that are used include graphene oxide, carbon nanotubes (CNTs), and metal nanoparticles.

This chapter provides a comprehensive understanding of the recent developments in the high*k* nanocomposites without detailing the complex mathematical models and formulas that have been excessively quoted in various books and reviews. We provide an understanding of the nanocomposites processing, strategies to optimize their dielectric properties, and various filler materials that have been recently used. This section also strives to provide a future perspective in the high-*k* nanocomposites and conclude with some summarized remarks about the topic.

2. Electrical properties

Currently, pure polymers such as biaxially oriented polypropylene (BOPP) are used in energy storage applications, because of their high breakdown strength and low cost. However, pure polymers suffer from low magnitudes of dielectric constant, which results in low performance for energy density applications [2]. To overcome low dielectric constant limitations, high dielectric constant electroceramic nanoparticles are used as filler materials. Generally, due to the small band gap in semiconductors, thermal excitation is responsible for the generation of charge carriers, while the band gap of dielectric materials is relatively large, so electrical contacts or an external sources are responsible for the injection of charge carriers. Transition from one band to another in dielectrics requires high energy [9]. Electrons present in the valence shell of an atom are responsible for the dielectric phenomena, which interacts with externally applied fields, such as an electric or magnetic field. In polar dielectrics, the +ve and -ve charges are responsible for the production of electric dipole, whereas nonpolar dielectric materials lack this inherent dipole at the zero electric field, so an external potential is applied to shift the electron cloud, resulting in dipole phenomena [10]. Despite the use of high-kceramics as filler materials in the development of nanocomposites, another approach is to introduce electrically conductive nanofillers. Such a device configuration has shown superior dielectric response; however, low breakdown strength and high dissipation factor both are disadvantages to be considered [11]. Ceramics became the backbone of the electronic industry after the discovery of ferroelectricity in these materials in 1946. Ferroelectricity was first observed in BT in the mid-1940s and since then, BT has become one of the most essential ferroelectric materials [12]. Before the discovery of BT, steatite, mica, MgTiO₃, CaTiO₃, and TiO₂ were widely used in capacitors. These materials exhibit $\varepsilon_r \le 100$, which limits their use in the industry of dielectric capacitors [13–15]. During World War II, the need of high dielectric constant materials increased in capacitor applications [16, 17]. Ferroelectric materials exhibit nonlinear dielectric polarization against an external E due to the presence of permanent dipoles [18]. The polarization in these materials increases with the increasing strength of E, which corresponds to the alignment of dipoles in an applied electric field. The state (P_s) in which the dipoles of the ferroelectrics align with the applied field is called saturation. The polarization decreases with the reduction of *E* as well as with the reversal of the applied field's direction, however, when the applied electric field is removed (E = 0), ferroelectric materials still exhibit some polarization. When the value of the field reaches to a certain point, the materials exhibit zero polarization, which is called coercive field (E_c). Dielectric properties of ferroelectric materials change significantly with temperature near T_c . Generally, magnitude of k increases with an increasing temperature below T_c , reaching a maximum value and then decreases with a further increase in temperature, for example, barium titanate $k \approx 2000$ at room temperature reaches 7000 at T_c (~120°C) [19, 20]. Due to the high dielectric constant of ceramic materials, they are deemed as an efficient filler material for energy storage applications.

An ideal dielectric material resists the flow of charge completely; only allowing displacement of charges, resulting in polarization. In a typical capacitor arraignment, when an alternating *E* is applied to an ideal dielectric, the current will carry the voltage by a phase angle of $\pi/2$ (i.e., 90°), where no power will be absorbed by the dielectric, and the capacitor will exhibit dielectric loss (tan δ = 0). On the other hand, the practical materials exhibit tan δ , and it is because the current-voltage phase angle is not exactly 90°; therefore, the current is slightly lagging behind. The angle and magnitude of the lag are defined as δ and tan δ , respectively. Dielectric losses are associated with various mechanisms occurring in materials, such as electronic polarization, ion vibration, deformation, and ion migration. Generally, dielectric loss in ceramics is due to ion migration. Temperature and frequency are important factors that influence tan δ [21]. Compared to dielectric ceramics, the low magnitudes of k and tan δ in polymer dielectrics are attractive for transistor applications and they can be used in the form of thin layers (nanometer layers) as they exhibit low leakage current and high breakdown strength, which contributes to the miniaturization of electrical devices. Table 1 summarizes the breakdown strength of some common polymers. Pure polymers are not suitable for high energy density applications because of their low dielectric constant.

Polymer	Dielectric strength (V/µm)	Polymer	Dielectric strength (V/µm)				
Polyethylene (LD)	200	Polypropylene (biaxially oriented)	200				
Polyethylene (HD)	200	Polystyrene	200				
Polyethylene (XL)	220	Poly(vinylidene fluoride)	10.2				
Polycarbonate	252	Polyester	300				
Polyimide	280	Epoxy resin	25–45				
Table 1. Dielectric strength of commonly used polymers [22].							

High dielectric constants in ceramics originated from ionic polarization, which is associated with the asymmetric migration of the central metal cation in the crystal lattice. In contrast, polymers exhibit various types of polarization, i.e., ionic, electronic, and orientation, that are responsible for their dielectric constants [23, 24]. Typically, depending on the nature of the material and applied field, at least one kind of polarization mechanism is present in dielectrics. Electronic polarization is induced in a dielectric material when subjected to an external electric field, where the electron cloud is displaced relative to the nucleus. This type of polarization may be stimulated in all dielectrics when they are placed under an external electric field. In ionic polarization, the cations and anions in an atom are displaced in opposite directions,

resulting in a net dipole moment. The magnitude of the dipole moment generated for each ion pair is equivalent to the product of relative displacement and respective ionic charges. This type of polarization occurs only in ionic materials. Orientation polarization occurs in materials that possess permanent dipole moments, and it is induced when these permanent dipoles align in the direction of an applied electric field. This type of polarization decreases with an increase of temperature [25].

Another polarization characteristic of the multicomponent dielectric systems (such as semicrystalline polymers, inorganic-organic nanocomposites, and polymer blends) is Maxwell-Wagner-Sillars (MWS) interfacial polarization (IP), which is associated with the reorganization of the interface charges, i.e., electrons and hole accumulated at the interfaces in a heterogeneous system. According to the MWS effect, when an electric field is applied to a heterogeneous dielectric system, the charges accumulate on the surfaces of the different dielectrics exhibiting different retention time. Such a configuration is desirable in achieving a high dielectric constant in the system. However, a drawback to this inhomogeneous distribution of charge in a multicomponent system is that the whole system may fail, therefore, it is important to optimize all the parameters that will define the final properties of the system for better performance [3].

3. Filler materials/polymers

The dielectric properties of polymer nanocomposites are affected by various factors such as the type, size, concentration, and shape of the filler materials and polymer matrix. For high energy density applications, the semiconductive fillers such as titanium dioxide (TiO₂), zinc oxide (ZnO), molybdenum sulfide (MoS₂), and silicon carbide (SiC) have been studied. These fillers have shown considerable promise as candidates for high voltage applications in polymer dielectrics [26]. Among these, TiO₂ presents excellent physiochemical properties and it can be crystallized in the form of rutile, anatase, and brookite structures. Tomara et al. [27] reported the processing of anatase TiO₂-epoxy resin nanocomposites. Various concentrations from 3 to 12% parts per hundred resins per weight were investigated. The broadband dielectric spectroscopy measurements showed five relaxation modes designated as γ , β , intermediate dipolar effect (IDE), α , and interfacial polarization (IP) with varying temperatures and constant frequencies. The γ and β modes were associated with the reorientation of smaller segments and rearrangement of the polarized groups. The IDE, α and IP were attributed to the TiO₂ inclusions, glass to rubber transitions, and electric heterogeneity of the nanocomposites, respectively. The TiO₂-polymer composites were reported to have a superior dielectric response compared to pure polymers [27]. Xie et al. [28] prepared core-shell structured hyperbranched aromatic polyimide grafted BaTiO₃ (BT-HBP) hybrid nanofillers. Poly(vinylideneflouride)-trifluoroethylene-chlorofluoethylene(PVDF-TrFE-CFE) was used as the polymer matrix. The dielectric study showed that the 40 vol% of BT-HBP had a high dielectric constant (1485.5 at 1000 Hz) compared to untreated BaTiO₃, which was recorded as 206.3 [28]. To further investigate and optimize the dielectric and energy storage properties of polymer nanocomposites, dielectric ceramics with perovskite structures are used as filler materials. **Table 2** presents various ceramic fillers and polymers with respective dielectric constants.

k	Polymers	k
1700	Nonfluorinated aromatic polyimides	3.2–3.6
2590	Fluorinated polyimide	2.6-2.8
225	Poly(phenyl quinoxaline)	2.8
2000	Poly(arylene ether oxazole)	2.6–2.8
~60,000	Poly(arylene ether)	2.9
~100,000	Polyquinoline	2.8
80	Silsesquioxane	2.8-3.0
25	Poly(norborene)	2.4
3.9	Perfluorocyclobutane polyether	2.4
9	Fluorinated poly(arylene ether)	2.7
22	Polynaphthalene	2.2
25	Poly(tetrafluoroethylene)	1.9
11	Polystyrene	2.6
15	Poly(vinylidene fluoride-co-hexafluoropropylene)	~12
30	Poly(ether ketone ketone)	~3.5
	x 1700 2590 225 2000 ~60,000 ~100,000 80 25 3.9 9 22 25 11 15 30	xForymers1700Nonfluorinated aromatic polyimides2590Fluorinated polyimide2590Fluorinated polyimide225Poly(phenyl quinoxaline)2000Poly(arylene ether oxazole)~60,000Poly(arylene ether)~100,000Polyquinoline80Silsesquioxane25Poly(norborene)3.9Perfluorocyclobutane polyether9Fluorinated poly(arylene ether)22Polynaphthalene25Poly(tetrafluoroethylene)11Polystyrene15Poly(vinylidene fluoride-co-hexafluoropropylene)30Poly(ether ketone ketone)

*PLZT, lead lanthanum zirconium titanate.

Table 2. Dielectric constant of commonly used ceramics and polymers for energy storage applications [22].

The problem associated with perovskite ceramics as fillers in polymer matrix is the low breakdown strength of the final system.Due to higher dielectric constant of the ceramic materials than polymers, a significant electric field is concentrated in the polymer matrix compared to the ceramic nanoparticles. This behavior is responsible for the decrease of breakdown strength in the ceramic-polymer nanocomposite systems. To address this issue, dielectric fillers with large aspect ratios, such as (1D) BaTiO₃, hexagonal boron nitride nanosheets, and (2D) clay nanosheets are used. These strategies are the tradeoff between the permittivity values and dielectric breakdown. These systems have shown high magnitudes of breakdown strength that may be due to the presence of order traps, an increase in the number of scattering traps to injected charges, and the path tortuosity in the electrical treeing process during breakdown [29]. Some recently used ceramic-polymer composites with their corresponding electrical properties are summarized in **Table 3**.

Fillers	Shape	Polymer	Surface modifier	HOD (J/cm ³)	E_b	Refs			
Ba _{0.6} Sr _{0.4} TiO ₃	nf	PVDF	_	6.8	3800 kV/cm	[30]			
$Ba_{0.6}Sr_{0.4}TiO_3$	nf	PVDF	Isopropyl dioleic (dioctylphosphate) titanate	6.95	3800 kV/cm	[31]			
Ba _{0.7} Sr _{0.3} TiO ₃	nw	(P(VDF–HFP))	Poly(pentafluorophenyl acrylate)	2.2	200 kV/mm	[32]			
BaTiO ₃	np	PDA	PLA	1.52	120 MV/m	[33]			
BaTiO ₃	np	PVDF	Hydroxylation	3.24	2.25 MV/cm	[34]			
$Ba_{1-x}Ca_xTiO_3$	np	PVDF	Hydroxylation	4.72	1.75 MV/cm	[34]			
$BaZr_{1-x}Ti_xO_3$	np	PVDF	Hydroxylation	7.74	2.5 MV/cm	[34]			
BaTiO ₃	np	PVDF	SiO ₂	6.28	340 MV/m	[35]			
BaTiO ₃	nc	P(VDF-HFP	NOBF ₄	4.66	150 MV/m	[36]			
BaTiO ₃	nf	PVDF	3-aminopropyltriethoxyilane	5.6	3300 kV/cm	[37]			
*nf nanofibers: nn nanonarticles: nc nanocubes									

Table 3. Energy density and breakdown strength of the ceramic-polymer nanocomposites recently reported in the literature.

Another complication associated with the nanocomposites is the high dielectric loss. To reduce the dielectric loss, a dielectric layer coated with conductive nanoparticles is artificially synthesized. Such efforts have been reported to be successful, however, a decrease in the dielectric constant was also observed. Moreover, the processing of such systems may cause conductive networks or tunneling effect between the conductive nanoparticles coated on the surface of the dielectric layer, which results in high dielectric loss and high current leakage. One method to overcoming this problem is to distribute the fillers in the polymer matrix homogeneously in order to avoid contact between the filler particles [38]. Another problem that may cause high current leakage, high dielectric loss, low dielectric constant, and low breakdown strength are the compatibility issues between the inorganic and organic nanocomposites. To resolve this problem, "all polymer" approach has been introduced, where a dielectric polymer such as PVDF and its derivatives are used in the form of polymer blends. These attempts have shown superior dielectric properties; however, these polymer blends are known to cause high dielectric loss. To further modify these systems, a "percolative" dielectric composite approach has been developed. In this method, a conductive organic domain is dispersed in a dielectric polymer matrix. The space charge accumulates at the interface of the conductive organic and dielectric domains. A high dielectric response is achieved because the conductive domain acts as the "super dipole", resulting in high polarization. The magnitude of the dielectric constant reaches a maximum, with an increasing volume fraction of the organic domain, up to just below the percolation threshold. All polymer systems have the advantage over inorganic-organic polymer composites, such as easy processing, economical, and light

weight; however, such systems also suffer from high leakage current and low breakdown strength [39].

The extensive studies that have been reported for various filler materials in the polymer matrix only highlight the advantages of the final systems. It is important to critically analyze the underlining physics and chemistry of the filler materials, polymer matrix, and the dielectric response of the multicomponent systems. An essential aspect of the reported results is the reproducibility for practical device performance.

4. Interfacial chemistry

The dielectric constant of the polymer nanocomposites can be increased by loading a high concentration of the dielectric constant fillers. However, high constant, i.e., BT (60%) leads to agglomeration of the filler particles in the polymer matrix, which results in pore formation and subsequently low dielectric constant and high dielectric loss. In order to homogeneous-ly load high concentration of the dielectric fillers, the interfacial chemistry between the filler particles and the polymer matrix must be optimized. Furthermore, the intergranular interaction should also be investigated for homogeneous distribution and conglomerates formed in the polymer matrix. Generally, the interfacial polarization is considered as the primary polarization mechanism in the polymer nanocomposites. The energy density capacity of the polymer nanocomposites can be increased by modifying the interfacial chemistry between the filler materials. By applying this technique, high magnitudes of dielectric constant and breakdown strength can be achieved. Therefore, for better performance of the device, surface interaction between the filler materials itself and the filler-polymer matrix is important [29]. To do so, it is vital to understand the affinity between the polymer matrix and filler particles.

One strategy for addressing this issue is modifying the surface of the filler materials. The surface modifier consists of two major components: the first one is the functional group that attaches the modifier to the filler particle's surface such as, $-PO_4^{3-}$, -OH, $-SO_3H^-$, $-SO_3^{2-}$, -COOH, $-NR_3^{z+}$, and $-Coo^-$; and the second component is the macromolecular chain, solvable and dispersible in different media such as polyether, polyester, polyolefin, and polyacrylate. For example, phosphoric acid and silane coupling agents are used for surface modification of the BT nanoparticles. Moreover, the molecular structure of the surface modifier must be given considerable attention, making sure it is similar to the polymer matrix; otherwise it will result in the formation of pores, voids, and cracks in the polymer nanocomposites. The problem of high leakage current and dielectric loss associated with the silane coupling agent is due to the unabsorbed residues species in the final system [40, 41]. Niu et al. [42] studied the relationship between the surface modifier structure and BT-PVDF nanocomposites for energy storage applications. The schematic surface modification, composites formation, and energy density graph are illustrated in **Figure 1**.

They reported the use of four types of modifiers which belong to the carboxylic acids, i.e., 2, 3, 4, 5-tetrafluorobenzoic acid, 4-(trifluoromethyl) phthalic acid, tetrafluorophthalic acid, and

phthalic acid designated as F4C, F3C2, F4C2, and C2, respectively. The breakdown strength was observed to improve in all four cases. The energy density of the BT/PVDF nanocomposites with F4C and C2 was increased by 35.7 and 37.7%, respectively [42]. Zhou et al. [43] studied the surface hydroxylated BT (h-BT)/PVDF nanocomposites, where crude BT (c-BT) nanoparticles were transferred to h-BT nanoparticles using the H₂O₂ aqueous solution. Results showed that h-BT presented high thermal stability, low frequency dependent dielectric response, low dielectric loss, and high magnitude of dielectric constant compared to c-BT-based nanocomposites [43]. Mukherjee et al. [44] reported a surface modification of the BT nanoparticles by using the plasma enhanced chemical vapor deposition (CVD) method, where the reactive amine groups were implemented as surface modification agents. The final modified nanoparticles were treated with epoxide monomers to form nanocomposites. A comparison between the modified BT/epoxide and the unmodified BT/epoxide nanocomposites showed that the former exhibited superior thermal and electrical properties to the latter [44].



Figure 1. Scheme process of nanoparticle modification and incorporation into the polymer matrix and discharged energy density of the nanocomposites filled with BT and m-BT nanoparticles [42].

Surface modifications of the filler material are important as it decreases the probability of contact between the filler materials, and it improves the compatibility between the fillers and the polymer matrix. Through this procedure, the properties of the polymer nanocomposites can be enhanced for energy storage applications.

5. Processing strategies

The dielectric and energy storage properties of the polymer nanocomposites can also be tuned through the preparation methods. The processing techniques not only include the composite formation, but also the synthesis of the filler materials in various sizes and shapes. This section only summarizes the methods for the formation of filler-polymer nanocomposites. The most adaptable synthesis approach for the processing of the polymer composites in the recent literature is liquid-phase assisted dispersion. In this method, the filler materials and the polymer are mixed in a desired solvent, followed by stirring for a long duration, i.e., 24 h for homogeneous mixing. The mixture is then transferred into a glass substrate, where the thickness of the film is maintained. The film is further dried at various desired temperatures and times in a vacuum/air atmosphere to remove the solvent, then annealed at desired temperatures, i.e., BT@TiO2-nanofibers-P (VDF-HFP) at 200°C/7 min and subsequently quenched in an ice bath [45]. Another approach is the solution casting method, where a polymer is dissolved in a suitable solvent and a predetermined weight-percent of the filler material is added to the solution. The solution is thoroughly mixed using an ultrasonic bath or a magnetic stirrer, and then spin coated on a glass substrate. The process is repeated until the desired thickness is achieved, then the film is annealed at some low temperature (~80°C) for crystallization, and the solvent is removed by thermal dehydration in an oven.

Xu et al. [46] processed a three-phase system using polyimide (PI), BT, and multiwall carbon nanotubes (MWCNTs) by the electrospinning technique. MWCNTs were homogeneously dispersed in the PI matrix and subsequently collected by using the BT particles. The solution was subjected to electrospinning using 20 kV/20 cm from the spinneret to the collector, keeping the flow rate of 1.2 mL/h at room temperature. The resultant nanofibers were treated with heat, at 70°C/6h (vacuum), 250°C/1 h in N₂. The composite nanofibers were further treated at 5 MPa pressure at 300°C in a vacuum for 5 min using hot-pressing techniques. A high dielectric constant of 1061.98 (at 100 Hz) and an energy density of 4.773 J/cm³ were recorded for the composition with 40 vol% BTNPs/10 vol% MWCNTs [46]. Zhang et al. [47] reported a novel strategy represented in Figure 2 for the processing of the BT and PVDF nanocomposites. Nanofibers were synthesized using electrospinning, and the surfaces were modified using 1H,1H,2H,2H-perfluorooctyl trimethoxysilane. Finally, the modified BT and PVDF nanocomposites were processed using solution blending, where the dielectric properties of the final composites were improved. In addition, this technique has an advantage over the grafting method for processing the nanocomposites due to its low cost and simple procedure [47].



Figure 2. Schematic illustration of preparation of the nanocomposites of PVDF and fluorosilane-modified BT nanofibers [47].

6. Future trends

To further enhance the dielectric response and physiochemical stability of the high-*k* dielectric nanocomposites is the fabrication of high aspect ratio filler materials. Tang et al. [48] studied the effect of different aspect ratios of the BT nanowires on the dielectric properties of the BT/PVDF nanocomposites. The aspect ratios of the nanowires were tuned by controlling the temperature during hydrothermal synthesis, where they were varied from 9.3 to 45.8 corresponding to the temperature ranges from 150 to 240°C, respectively. A direct relationship was observed with the aspect ratio of nanocomposites and dielectric constant. A high dielectric constant of 44.3 was reported for the BT-30 vol% nanocomposites with an aspect ratio of 45.8, which was 30.7% higher than BT samples with an aspect ratio of 9.3 while 352% higher than polymer matrix samples [48]. Despite the high dielectric constant fillers for high dielectric nanocomposite applications, such as BT and PbZrTiO₃-based derivatives, these filler materials still suffer from some disadvantages, which include low dielectric response even with high loading concentration, low breakdown strength, and deteriorated flexibility. Furthermore, lead-based compounds are toxic in nature and are expected to be banned in the near future. An alternative to ceramic fillers is the graphenebased nanocomposites for high-energy and ultracapacitor applications. Graphene is a one atom thick sheet of carbon, in which carbon atoms exhibit sp² hybridization which correspond to excellent electron mobility, mechanothermal stability, and high flexibility. Graphene oxide (GO) can be easily dispersed in the aqueous solution and the electrical properties can be optimized by using various thermal and chemical approaches such as partial reduction. Thus, the GO/polymer nanocomposites can prove an efficient system for high dielectric applications [49, 50]. Recently, attention has been given to the carbon nanotubes (CNTs), a crystalline form of carbon because of their unique physical and mechanical properties. CNTs are considered to be potential candidates for the formation of nanocomposites, which can improve their electrical, thermal, and mechanical properties [51]. Although extensive studies have reported the dielectric properties of the nanocomposites, very few investigate the dielectric properties vs. temperature [52]. These properties must be thoroughly investigated under mechanical and dielectric thermal stability for practical device applications. Recent advances in the computational material science, physics, and chemistry have developed sophisticated algorithms for predicting the physical and chemical properties of the system. These methods and molecular dynamic techniques must be utilized to design a more reliable and comprehensive system for energy storage applications.

7. Conclusions

For high-energy-density applications, materials should exhibit the high-energy storage capacity. For this purpose, materials should demonstrate high dielectric permittivity, low leakage current, low dielectric loss, and high breakdown strength. All these parameters are crucial for implementing laboratorial research in industrial processes. Furthermore, an economical device fabrication strategy should be adopted for practical and commercial applications; however, a single material does not ideally express all these properties as one system; therefore, a tradeoff is used for device performance between the material properties for different applications. From previous discussion, it has been established that the energy storage capability of the dielectric nanocomposites is strongly influenced by the choice of filler materials, shape and size, morphology, processing methods, use of surfactants or surface modifying agents, and polymer matrix. For better storage applications, all these parameters must be optimized and new strategies should be developed for better processing and understanding of the device fabrications.

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References

- [1] X. Huang, P. Jiang, Core-shell structured high-k polymer nanocomposites for energy storage and dielectric applications, Advanced Materials, 27 (2015) 546–554.
- [2] Q. Li, K. Han, M.R. Gadinski, G. Zhang, Q. Wang, High energy and power density capacitors from solution-processed ternary ferroelectric polymer nanocomposites, Advanced Materials, 26 (2014) 6244–6249.
- [3] J. Yuan, S. Yao, P. Poulin, Dielectric Constant of Polymer Composites and the Routes to High-k or Low-k Nanocomposite Materials, Polymer Nanocomposites: Electrical and Thermal Properties, Springer, Switzerland, 2016.
- [4] S. Webb, I. Ian Jackson, J.F. Gerald, Viscoelasticity of the titanate perovskites CaTiO₃ and SrTiO₃ at high temperature, Physics of the Earth and Planetary Interiors, 115 (1999) 259–291.
- [5] V. Mathivanan, M. Haris, Studies on solution-grown pure and doped sodium potassium tartrate crystals, Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy, 102 (2013) 341–349.
- [6] C. Eckart, Principle of Underwater Sound, (Ed.), Wakefield, Massachusetts, 1946.
- [7] M.D. Toomey, K. Gao, G.P. Mendis, E.B. Slamovich, J.A. Howarter, Hydrothermal synthesis and processing of barium titanate nanoparticles embedded in polymer films, ACS Applied Materials & Interfaces, 7 (2015) 28640–28646.
- [8] M. Zhu, X. Huang, K. Yang, X. Zhai, J. Zhang, J. He, P. Jiang, Energy storage in ferroelectric polymer nanocomposites filled with core-shell structured polymer@BaTiO₃ nanoparticles: understanding the role of polymer shells in the interfacial regions, ACS
 Applied Materials & Interfaces, 6 (2014) 19644–19654.
- [9] G.N. Gerasimov, L.I. Trakhtenberg, Chapter 10 Vapor Deposited Composite Films Consisting of Dielectric Matrix with Metal/Semiconductor Nanoparticles, 1st ed., Elsevier, USA, 2007.
- [10] K. Heileman, J. Daoud, M. Tabrizian, Dielectric spectroscopy as a viable biosensing tool for cell and tissue characterization and analysis, Biosensors & Bioelectronics, 49 (2013) 348–359.
- [11] K. Yang, X. Huang, L. Xie, C. Wu, P. Jiang, T. Tanaka, Core-shell structured polystyrene/BaTiO₃ hybrid nanodielectrics prepared by in situ RAFT polymerization: a route to high dielectric constant and low loss materials with weak frequency dependence, Macromolecular Rapid Communications, 33 (2012) 1921–1926.

- [12] A. Mahmood, A. Naeem, Y. Iqbal, T. Mahmood, A. Ullah, Electrical characterization of Mn doped-(Ba_{0.3}Sr_{0.7})Mnx(Ti_{0.9}Zr_{0.1})_{1-x}O₃ ceramics, Materials Research Bulletin, 72 (2015) 13–19.
- [13] I. Apostol, K.V. Saravanan, C.J.A. Monty, P.M. Vilarinho, Solar physical vapor deposition: a new approach for preparing magnesium titanate nanopowders, Applied Surface Science, 285 (2013) 49–55.
- [14] A. Ullah, Y. Iqbal, T. Mahmood, A. Mahmood, A. Naeem, M. Hamayun, Kinetic analysis on the synthesis of Mg_{0.95}Zn_{0.05}TiO₃ microwave dielectric ceramic by polymeric precursor method, Ceramics International, 41 (2015) 15089–15096.
- [15] E.E.C. Oliveira, A.G. D'Assuncao, J.B.L. Oliveira, A.M. Cabral, Small size dual-band rectangular dielectric resonator antenna based on calcium titanate (CaTiO₃), Microwave and Optical Technology Letters, 54 (2012) 976–979.
- [16] I.S. Seo, W.S. Chin, D.G. Lee, Characterization of electromagnetic properties of polymeric composite materials with free space method, Composite Structures, 66 (2004) 533–542.
- [17] S.M. Abbas, M. Chandra, A. Verma, R. Chatterjee, T.C. Goel, Complex permittivity and microwave absorption properties of a composite dielectric absorber, Composites Part A: Applied Science and Manufacturing, 37 (2006) 2148–2154.
- [18] Q.-D. Ling, D.-J. Liaw, C. Zhu, D.S.-H. Chan, E.-T. Kang, K.-G. Neoh, Polymer electronic memories: materials, devices and mechanisms, Progress in Polymer Science, 33 (2008) 917–978.
- [19] G. Schileo, Recent developments in ceramic multiferroic composites based on core/shell and other heterostructures obtained by sol-gel routes, Progress in Solid State Chemistry, 41 (2013) 87–98.
- [20] E. Sun, W. Cao, Relaxor-based ferroelectric single crystals: growth, domain engineering, characterization and applications, Progress in Materials Science, 65 (2014) 124–210.
- [21] L.B. Kong, T.S.Z. S. Li, J.W. Zhai, F.Y.C. Boey, J. Ma, Electrically tunable dielectric materials and strategies to improve their performances, Progress in Materials Science, 55 (2010) 840–893.
- [22] P. Barber, S. Balasubramanian, Y. Anguchamy, S. Gong, A. Wibowo, H. Gao, H.J. Ploehn, Z.L. Hans-Conrad, Polymer composite and nanocomposite dielectric materials for pulse power energy storage, Materials, 2 (2009) 1697–1733.
- [23] B.C. Riggs, S. Adireddy, C.H. Rehm, V.S. Puli, R. Elupula, D.B. Chrisey, Polymer nanocomposites for energy storage applications, Materials Today: Proceedings, 2 (2015) 3853–3863.

- [24] A. Naeem, A. Mahmood, Y. Iqbal, A. Ullah, T. Mahmood, M. Humayun, Dielectric and impedance spectroscopic studies on (Ba_{0.5}Sr_{0.5})Mn_x(Ti_{0.95}Fe_{0.05})_{1-x}O₃ ceramics synthesized by using sol–gel method, Journal of Alloys and Compounds, 645 (2015) 290–296.
- [25] Z.-G. Ye, Handbook of Advanced Dielectric, Piezoelectric and Ferroelectric Materials: Synthesis, Properties and Applications. Woodhead Publishing Limited, England. Cambridge, 2008.
- [26] Q. Jia, X. Huang, G. Wang, J. Diao, P. Jiang, MoS₂ nanosheet superstructures based polymer composites for high-dielectric and electrical energy storage applications, The Journal of Physical Chemistry C, 120 (2016) 10206–10214.
- [27] G.N. Tomara, A.P. Kerasidou, A.C. Patsidis, P.K. Karahaliou, G.C. Psarras, S.N. Georga, C.A. Krontiras, Dielectric response and energy storage efficiency of low content TiO₂-polymer matrix nanocomposites, Composites Part A: Applied Science and Manufacturing, 71 (2015) 204–211.
- [28] L. Xie, X. Huang, Y. Huang, K. Yang, P. Jiang, Core-shell structured hyperbranched aromatic polyamide/BaTiO₃ hybrid filler for poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) nanocomposites with the dielectric constant comparable to that of percolative composites, ACS Applied Materials & Interfaces, 5 (2013) 1747–1756.
- [29] X. Zhang, Y. Shen, Q. Zhang, L. Gu, Y. Hu, J. Du, Y. Lin, C.W. Nan, Ultrahigh energy density of polymer nanocomposites containing BaTiO₃@TiO₂ nanofibers by atomicscale interface engineering, Advanced Materials, 27 (2015) 819–824.
- [30] S. Liu, S. Xue, W. Zhang, J. Zhai, G. Chen, The influence of crystalline transformation of Ba_{0.6}Sr_{0.4}TiO₃ nanofibers/poly(vinylidene fluoride) composites on the energy storage properties by quenched technique, Ceramics International, 41 (2015) S430–S434.
- [31] Z.B. Pan, L.M. Yao, J.W. Zhai, S.H. Liu, K. Yang, H.T. Wang, J.H. Liu, Fast discharge and high energy density of nanocomposite capacitors using Ba_{0.6}Sr_{0.4}TiO₃ nanofibers, Ceramics International, 42 (2016) 14667–14674.
- [32] S. Wang, X. Huang, G. Wang, Y. Wang, J. He, P. Jiang, Increasing the energy efficiency and breakdown strength of high-energy-density polymer nanocomposites by engineering the Ba_{0.7}Sr_{0.3}TiO₃ nanowire surface via reversible addition-fragmentation chain transfer polymerization, The Journal of Physical Chemistry C, 119 (2015) 25307–25318.
- [33] Y. Fan, X. Huang, G. Wang, P. Jiang, Core-shell structured biopolymer@BaTiO₃ nanoparticles for biopolymer nanocomposites with significantly enhanced dielectric properties and energy storage capability, The Journal of Physical Chemistry C, 119 (2015) 27330–27339.
- [34] S. Adireddy, V.S. Puli, T.J. Lou, R. Elupula, S.C. Sklare, B.C. Riggs, D.B. Chrisey, Polymer-ceramic nanocomposites for high energy density applications, Journal of Sol-Gel Science and Technology, 73 (2014) 641–646.

- [35] K. Yu, Y. Niu, Y. Bai, Y. Zhou, H. Wang, Poly(vinylidene fluoride) polymer based nanocomposites with significantly reduced energy loss by filling with core-shell structured BaTiO₃/SiO₂ nanoparticles, Applied Physics Letters, 102 (2013) 102903.
- [36] S.S. Parizi, A. Mellinger, G. Caruntu, Ferroelectric barium titanate nanocubes as capacitive building blocks for energy storage applications, ACS Applied Materials & Interfaces, 6 (2014) 17506–17517.
- [37] S. Liu, S. Xue, W. Zhang, J. Zhai, Enhanced dielectric and energy storage density induced by surface-modified BaTiO₃ nanofibers in poly(vinylidene fluoride) nanocomposites, Ceramics International, 40 (2014) 15633–15640.
- [38] S. Luo, S. Yu, R. Sun, C.P. Wong, Nano Ag-deposited BaTiO₃ hybrid particles as fillers for polymeric dielectric composites: toward high dielectric constant and suppressed loss, ACS Applied Materials & Interfaces, 6 (2014) 176–182.
- [39] M.S. Islam, Y. Qiao, C. Tang, H.J. Ploehn, Terthiophene-containing copolymers and homopolymer blends as high-performance dielectric materials, ACS Applied Materials & Interfaces, 7 (2015) 1967–1977.
- [40] N. Kamezawa, D. Nagao, H. Ishii, M. Konno, Transparent, highly dielectric poly(vinylidene fluoride) nanocomposite film homogeneously incorporating BaTiO₃ nanoparticles with fluoroalkylsilane surface modifier, European Polymer Journal, 66 (2015) 528–532.
- [41] H. Luo, D. Zhang, C. Jiang, X. Yuan, C. Chen, K. Zhou, Improved dielectric properties and energy storage density of poly(vinylidene fluoride-co-hexafluoropropylene) nanocomposite with hydantoin epoxy resin coated BaTiO₃, ACS Applied Materials & Interfaces, 7 (2015) 8061–8069.
- [42] Y. Niu, Y. Bai, K. Yu, Y. Wang, F. Xiang, H. Wang, Effect of the modifier structure on the performance of barium titanate/poly(vinylidene fluoride) nanocomposites for energy storage applications, ACS Applied Materials & Interfaces, 7 (2015) 24168–24176.
- [43] T. Zhou, J.W. Zha, R.Y. Cui, B.H. Fan, J.K. Yuan, Z.M. Dang, Improving dielectric properties of BaTiO₃/ferroelectric polymer composites by employing surface hydroxylated BaTiO₃ nanoparticles, ACS Applied Materials & Interfaces, 3 (2011) 2184–2188.
- [44] N. Mukherjee, D. Wavhal, R.B. Timmons, Composites of plasma surface functionalized barium titanate nanoparticles covalently attached to epoxide matrices: synthesis and evaluation, ACS Applied Materials & Interfaces, 2 (2010) 397–407.
- [45] X. Zhang, Y. Shen, B. Xu, Q. Zhang, L. Gu, J. Jiang, J. Ma, Y. Lin, C.W. Nan, Giant energy density and improved discharge efficiency of solution-processed polymer nanocomposites for dielectric energy storage, Advanced Materials, 28 (2016) 2055–2061.
- [46] W. Xu, Y. Ding, S. Jiang, L. Chen, X. Liao, H. Hou, Polyimide/BaTiO₃/MWCNTs threephase nanocomposites fabricated by electrospinning with enhanced dielectric properties, Materials Letters, 135 (2014) 158–161.

- [47] X. Zhang, Y. Ma, C. Zhao, W. Yang, High dielectric constant and low dielectric loss hybrid nanocomposites fabricated with ferroelectric polymer matrix and BaTiO₃ nanofibers modified with perfluoroalkylsilane, Applied Surface Science, 305 (2014) 531–538.
- [48] H. Tang, Z. Zhou, H.A. Sodano, Relationship between BaTiO₃ nanowire aspect ratio and the dielectric permittivity of nanocomposites, ACS Applied Materials & Interfaces, 6 (2014) 5450–5455.
- [49] S.Cho, J.S.Lee, J.Jang, Poly(vinylidenefluoride)/NH₂-treated graphenenanodot/reduced graphene oxide nanocomposites with enhanced dielectric performance for ultrahigh energy density capacitor, ACS Applied Materials & Interfaces, 7 (2015) 9668–9681.
- [50] M. Yasin, T. Tauqeer, S.M.H. Zaidi, S.E. San, A. Mahmood, M.E. Köse, B. Canimkurbey, M. Okutan, Synthesis and electrical characterization of graphene oxide films, Thin Solid Films, 590 (2015) 118–123.
- [51] C.-C. Wu, C.-C. Su, C.-F. Yang, Preparation, structure and properties of carbon nanotube reinforced polymer nanocomposites, Synthetic Metals, 205 (2015) 98–105.
- [52] M. Rajib, M. Arif Ishtiaque Shuvo, H. Karim, D. Delfin, S. Afrin, Y. Lin, Temperature influence on dielectric energy storage of nanocomposites, Ceramics International, 41 (2015) 1807–1813.





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