Chapter-I

Introduction and Literature Review

1.1 Introduction

The growing demand for energy, combined with the diminishing availability of fossil fuels, necessitates an increase in energy efficiency and a shift towards sustainable and renewable energy sources. This has led to an expansion in the development of renewable energy technologies, particularly those involving solar and wind power. Given the variability in production and consumption patterns of these energy sources, it is critical to invest in new, cost-effective and eco-friendly energy storage solutions including fuel cells, batteries, electrochemical supercapacitors and dielectric capacitors[11–14]. These devices can be categorized mainly in two categories namely long-term storage and short-term storage devices. Batteries are in long term storage category that have high energy storage density and low power density, thus its application in power electronics application is limited. On other hand, dielectric capacitors are short term energy storage devices due to its low energy storage density and high-power density, which is a result of their rapid energy absorption and release capabilities This characteristics positions them as a promising solution in the area of power electronics applications like medical devices, hybrid electric vehicles and electrical weapon systems[15–18]. However, the low energy storage density of capacitors using conventional dielectrics remains a significant obstacle towards these potential applications[19–23]. In general, the energy storage density (U_e) of a dielectric material is equivalent to the integral:

$$U_e = \int_0^{Pm} E dP \qquad 1.1$$

where E is the electric field and P_m is the maximum electric polarization. For linear dielectric like polymers and their composites, the above equation can be expressed as:

$$U_e = \frac{1}{2}\varepsilon_0\varepsilon_r E_b^2 \qquad 1.2$$

In this equation, ε_r is the relative dielectric permittivity, ε_0 is the permittivity of free space and E_b is the electrical breakdown strength of the material. The dielectric permittivity in linear dielectrics remains unchanged regardless of the electric field applied. The energy storage capability is governed by the maximum electric field that can exert a capacitor without going breakdown is known as dielectric breakdown strength (E_b). Thus, it is very crucial to develop electroactive materials having low dielectric loss, high dielectric permittivity and high dielectric breakdown strength to enhance the energy storage density of a dielectric capacitor. Supercapacitors have complicated physical structure with limited maximum operating voltage are not much suitable material in above application. Traditional dielectric materials like ceramics have high dielectric permittivity, high stiffness and excellent thermal stability[24–26] but their practical use in high energy storage density capacitors is severely limited due to their low dielectric breakdown strength, high density, low flexibility and difficult synthesis conditions[14,27]. The application field of conventional dielectric capacitors can be highly expanded if their energy storage capacity can compete with batteries or even electrochemical supercapacitors as can be seen in Fig. 1.1. Compared to traditional ceramics, polymer dielectrics have relatively high dielectric breakdown strength and processing advantages like mechanical flexibility and ability to be molded into various configurations for power electronic applications having reduced weight and volume[28–31]. However, most of the polymers could not fulfill the rising demands for high energy storage density capacitor applications because of their intrinsic low dielectric permittivity ($\sim \varepsilon_r < 10$). This could lead to a strong dependence of the high energy storage density in polymers on a high applied external electric field ($E > 5000$ KV/cm)[23,32]. Therefore, a key challenge is to significantly increase the dielectric permittivity of polymers preserving their other excellent physical properties. Thus, higher energy storage density may be attained via synthesizing polymer-based nanocomposite dielectric materials.

Polymer based nanocomposite materials having high dielectric constant and large dielectric breakdown strength is supposed to be more potential in this area.

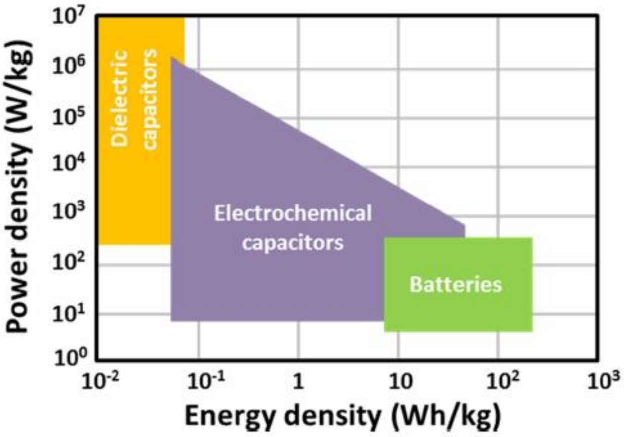

Fig. 1.1 Ragone plot representing energy density and power density of dielectric capacitors, Electrochemical supercapacitors and batteries [33].

1.2 Ceramics in perovskite structure

The perovskite oxide name originates from the mineral name “perovskite” of the natural mineral calcium titanate ($CaTiO_3$) and is represented by basic formula ABO_3. The ideal perovskite structure possess cubic crystal structure with Pm3m space group (No- 221). The ions in the Pm3m space group occupy Wyckoff position at A(0,0,0), B(1/2,1/2,1/2) and O(0,1/2,1/2). In ideal cubic perovskite structure, larger cation A are located at the centre of cubo-octahedron and smaller cation B are located at the centre of octahedron formed by the O ions. The perovskite structure may be found in tetragonal, cubic, orthorhombic, monoclinic or rhombohedral forms depending upon the ionic radii of anion and cations[34]. The cubic unit cell of perovskite structure is shown in Fig. 1.2.

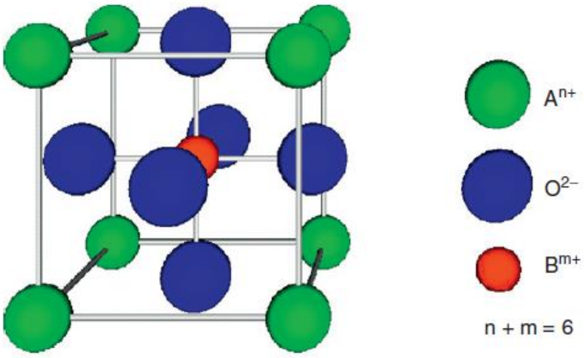

Fig. 1.2 Unit cell of Perovskite structure with general formula ABO_3 [35].

In the unit cell, large cation A is at the corners, small cation B is at the body centered position and O anion is at the face centered position of cubic unit cell. The structure of perovskite is decided by short range forces between adjacent ions and long-range electrostatic interaction among unit cells. In 1962, Goldschmidt introduced a parameter namely tolerance factor (t) to precisely characterize the stability of the perovskite structure[36]. The tolerance factor (t) is related with ionic radius and can be determined with the concept of theory on close packed structures. The tolerance factor (t) is represented by

$$t = \frac{(R_A+R_O)}{\sqrt{2}(R_B+R_O)} \tag{1.3}$$

where t is the tolerance factor and R_A, R_O, R_B is the ionic radius of A cation, oxygen (usually anion) and B cation respectively. The value of tolerance factor (t) lies in the range $0.8 < t < 1.05$ for a stable perovskite structure. There are three possibilities in case of tolerance factor (t)

- $t = 1$: Perovskite structure is ideal cubic structure.
- $t > 1$: The B atom is too small for oxygen octahedron, thus displacive distortion will happen within BO_6 octahedron which gives rise to dipole moment. Thus perovskite will represent tetragonal structure.

- t < 1: The A atom is small for oxygen cubo-octahedron and can not effectively bonded with all 12 neighbouring O atoms. Thus tilting or rotation of BO_6 octahedron takes place which results in lower symmetry or distorted perovskite structure like orthorhombic or rhombohedral structure[37].

In ABO_3 type perovskite structure, substitutions are possible on A and B cation sites. Perovskite structure allows for various substitutions which are determined by the ionic radius and valency of dopants. For ABO_3 type stoichiometric compounds, the sum of valency of A and B cations must be equal to 6. The perovskite structure substitutions can be categorized into three main groups.

- **Isovalent substitutions:**

In this case, substituted and substituting ions should be of same valency. In this category, it is possible to have substitution exclusively on the A site, substitution exclusively on the B site or simultaneous substitution on the both A and B sites.

- **Heterovalent substitutions:**

If the substituted ions have different valency than substituting ions, then this is known as heterovalent substitution. In this case, only simultaneous substitution on both A and B sites are possible such that electrical charge neutrality is maintained by the anions and cations.

1.3 Fundamentals of dielectric capacitor

Dielectrics are a class of materials that exhibit polarization when subjected to an external electric field allowing the presence of electrostatic field within them[38,39]. Insulators are a type of dielectric materials that are used to prevent charge flow or leakage currents in electrical devices. Dielectrics have very low conductivity and energy band gap approximately higher than 3 eV. When a dielectric material is subjected to an external electric field, positive charges move in the direction of the external field while negative charges move in the opposite direction. This results in the separation of positive and negative charges within the material, yet the dielectric as a whole maintains a neutral state. Throughout this process, electron clouds shift from their equilibrium positions to shorter distances than atomic diameters, and migration of charge do not happen macroscopically, as is observed in conductors[40].

The electric dipole moment (μ) for a collection of charges is determined by multiplying the vector (r) extending from the center of the negative charges to positive charges by the absolute value of either positive or negative charges (q). This can be expressed as[40]

$$\mu = qr \qquad 1.4$$

The polarization (P) of a dielectric material is characterized as the overall dipole moment (M) per unit volume of the dielectric material and can be expressed as follows:

$$P = \frac{M}{V} \qquad 1.5$$

where V is the total volume of dielectric material and M is the total dipole moment.

Electric displacement represents total surface charge density due to an applied external electric field and is represented by the equation1.6 [41–43]

$$D = \varepsilon_0 E + P \qquad 1.6$$

where ε_0 represents the permittivity of free space, while D and P denote the electric displacement and polarization respectively of a dielectric material.

When a dielectric material is placed between the plates of a parallel plate capacitor under constant voltage, the electric displacement is solely associated with the free charges present at the electrodes. Polarization is specifically linked to the induced charges at the edge surface of the dielectric material. The electric field is associated with both free and induced charges. The static dielectric constant serves as a distinctive property of the dielectric material, and it is connected to the electric field, electric displacement, and polarization through equation 1.7.

$$\varepsilon_r = \frac{D}{\varepsilon_0 E} = 1 + \frac{P}{\varepsilon_0 E} = 1 + \chi \qquad 1.7$$

where parameter χ denotes the extent of polarization generated by a particular applied electric field, referred to as electric susceptibility. Meanwhile, ε_r represents the dielectric constant of the material, indicating the rate at which a dielectric material undergoes polarization. In the case of nonlinear dielectric materials, when the polarization (P) significantly exceeds the product of vacuum permittivity (ε_0) and the applied electric field (E), i.e., $P >> \varepsilon_0 E$, the polarization is nearly equivalent to the electric displacement (D).

In general, atoms do not have permanent electric dipole moment because of their spherical symmetry. However, if an external electric field is applied, atoms become polarized due to rearrangement of the electron cloud and there is generation of induced dipole moment in the direction of external electric field. When it is applied on polar molecules, it try to be oriented in the direction of external electric field due to the applied moment on it. Molecules represent deviation from the perfect orientation of the molecules because of thermally induced motion of the molecules. Polar molecules under applied electric field, behave as dipoles being oriented in local electric field direction and a deviation from the perfect orientation is observed due to the interaction of permanent and induced dipoles that can be seen in Fig. 1.3.

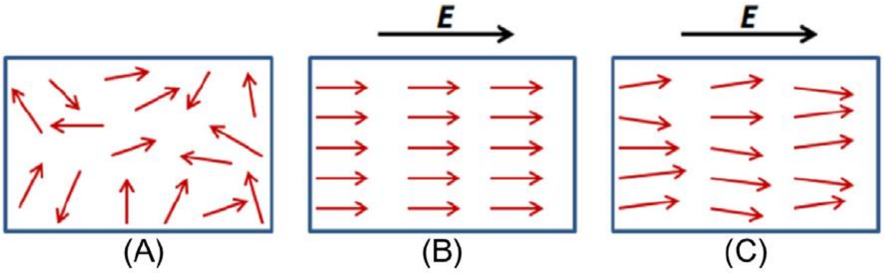

Fig. 1.3 Alignment of permanent dipoles under various conditions: (A) without an external electric field, (B) when subjected to an electric field without molecular interaction, and (C) when exposed to an electric field with molecular interaction [40].

The dielectric permittivity of any dielectric material placed into a parallel plate capacitor is the measure of the ability of dielectric material to store electrical energy when charging of plates is over[44]. This energy is stored in the form of permanent or induced polarization of the dielectric medium. This polarization may originate due to alignment of permanent dipoles in the dielectric medium parallel to each other in the opposite direction of external electric field and due to generation of induced polarization by the presence of the applied external electric field[45]

Dielectric losses are also associated with the dielectric material and is represented by tan δ which is defined as dissipation of electrical energy due to various physical processes. The dielectric permittivity has real as well as imaginary components and expressed by equation 1.8.

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad 1.8$$

dielectric loss or dissipation factor is given by

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad 1.9$$

The measurement of dielectric constant and dielectric loss of the materials can be performed using impedance analyzer. The dielectric property of materials directly depend on their value of polarization. The ability of a dielectric material to become polarized on application of external electric field is expressed by a microscopic electrical parameter known as polarizability or coefficient of polarization (α) and is given by[42,43]

$$P = \alpha E \qquad 1.10$$

There are two primary forms of polarizability: distortional, also known as deformational polarizability, and dipolar, referred to as orientational polarizability. Distortional polarizability is further categorized into electronic (α_e) and ionic (α_i) polarizability. Both fall under the same classification due to their common feature of exhibiting relative displacements of charges when subjected to an external electric field. Deformational polarization, along with its associated polarizabilities, remains unaffected by temperature, resulting in no energy loss.

Generally, orientational or dipolar polarizability (α_{or}) is present in polar dielectrics that possess a permanent dipole moment due to the molecular and group structures. Under the influence of an external electric field, the dipoles align in the direction of the field, deviating from their initial random orientation. Polymers typically comprise various polar groups and the orientation of occurring dipoles is the cumulative effect of all these polar groups. The dielectric properties of polar solids exhibit temperature dependence due to the varying degree of disorder in the motion of polar groups. Distortional and orientational polarizability are related to charges locally bound to atoms or molecules. Generally, charge carriers capable of migration within the dielectric contribute to polarization. However, the motion of these charges is impeded at interfaces or grain boundaries. This accumulation of polarization is termed as space charge polarization, resulting in an increase in the capacitance of the dielectric material. Consequently, a fourth term known as space charge or interfacial polarizability (α_{sc}) should be included in the total polarizability (α) expression for a dielectric material, which can be formulated as follows:

$$\alpha = \alpha_e+\alpha_i+\alpha_{or} + \alpha_{sc} \qquad 1.11$$

In the presence of above discussed polarization mechanism, the average dipole moment per molecule can be determined by

$$P = \alpha_e E_{loc} + \alpha_i E_{loc} + \alpha_{or} E_{loc} \qquad 1.12$$

Where E_{loc} is the local field which is given by

$$E_{loc} = E\frac{P}{3\varepsilon_0} \qquad 1.13$$

Here, It should be remembered that contribution of space charge polarization can not be included to the average value of dipole moment per molecule of bulk material because it happens at the interfaces or grain boundaries and local fields are not well defined there[42,43]. In general, there are four different types of polarization mechanism associated with dielectric material which are listed below:

(1) Electronic polarization

(2) Ionic polarization

(3) Dipolar or orientational polarization

(4) Space charge or interfacial polarization

Here, we shall further discuss each type of polarization mechanism in detail.

- **Electronic Polarization:**

In dielectric material, most of the electrons are bound to the nucleus of atom and these bound electrons are displaced when subjected to an external electric field, hence centre of positive charges of nucleus and negative charges of electron clouds are separated and electric dipoles are created. Thus, each atoms are characterized by electronic polarizability and this phenomenon is known as electronic polarization. Covalently bonded atoms have high dielectric constant due to this polarization mechanism. The electronic polarizability rises with an increasing number of electrons due to the loosely bound nature of outermost shell electrons to the nucleus. Fig. 1.4 shows phenomenon of electronic polarization.

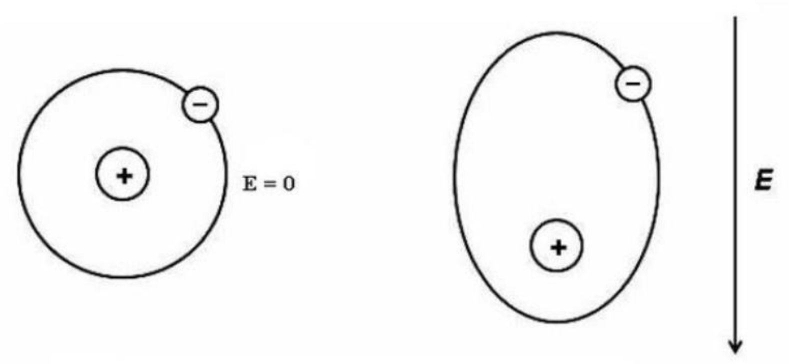

Fig. 1.4 Electronic polarization of an atom in presence of electric field [46].

- **Ionic Polarization:**

Ionic polarization arises due to the displacement of anions and cations of an ionic solid from its original position in opposite direction on applying external electric field. Each pair of oppositely charged neighbouring ions have permanent dipole moment even without external electric field. The Fig. 1.5 represents ionic polarization inside the crystal having chain of alternating anions and cations. The solid has no net polarization without an external electric field due to neutralization of equal magnitude and opposite direction of dipole moment of neighbouring dipoles. When we apply the external electric field, anions and cations are forced to move in opposite direction which results in net polarization nonzero. Thus, ionic polarization is electric field dependent and is larger than electronic polarization.

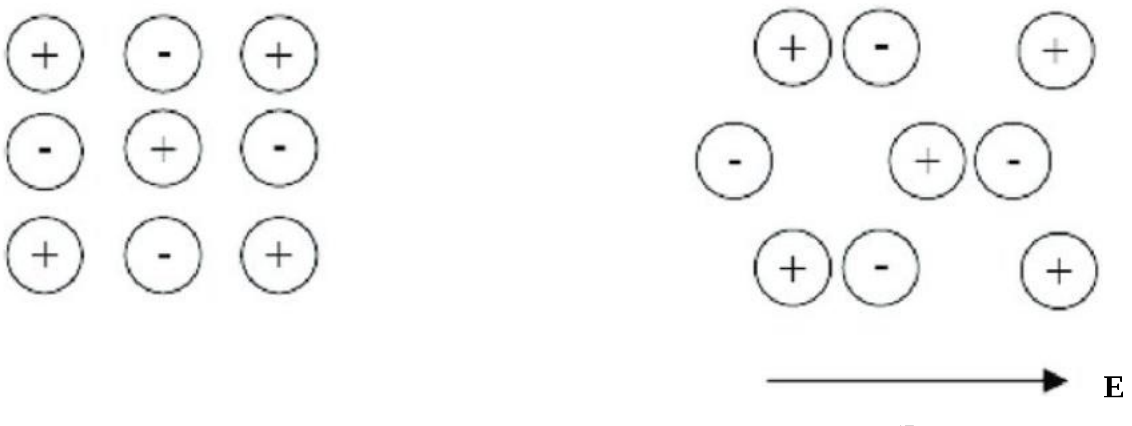

Fig. 1.5 Ionic Polarization in presence of electric field [47].

- **Dipolar or Orientational polarization:**

Orientational polarization is observed in that type of materials which have covalent bond of ionic character, a partial ionic bond and permanent dipole moment. The existence of permanent dipole moment is due to molecular geometry. The existence of an external electric field induces a torque on the dipoles, causing them to align with the direction of the external electric field. The alignment of these dipoles in the direction of the external electric field adds to the overall polarization, referred to as orientational polarization and is shown in Fig. 1.6. This polarization is temperature dependent and decreases with increasing temperature. PVDF based ferroelectric polymers also have permanent dipole moment and shows orientational polarization. C-F bonds exhibit a permanent dipole moment and align themselves in the direction of an external electric field when subjected to such a field. β phase of PVDF has spontaneous orientational polarization.

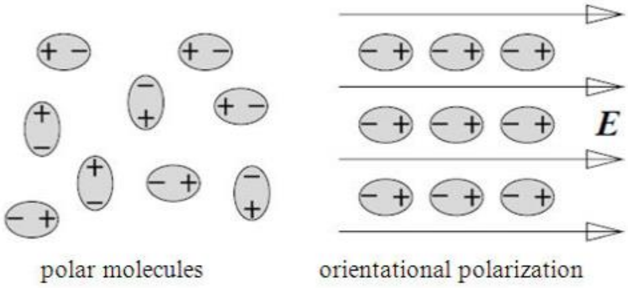

Fig. 1.6 Orientational Polarization under the influence of an electric field [48].

- **Interfacial or space charge polarization:**

Interfacial polarization, commonly referred to as space charge polarization, is predominantly observed in multiphase materials. It occurs as a result of the build-up of charges at the interface between two materials with varying conductivity levels. Electrons, holes, ions etc charge carriers may be trapped in the lattice vacancy, crystal defects, impurities or at the interface of two phases of the material. In this condition, space charges will be created which will affect the total polarization and average dielectric constant of the material. Fig. 1.7 represents mechanism of interfacial polarization that can occur in a dielectric material.

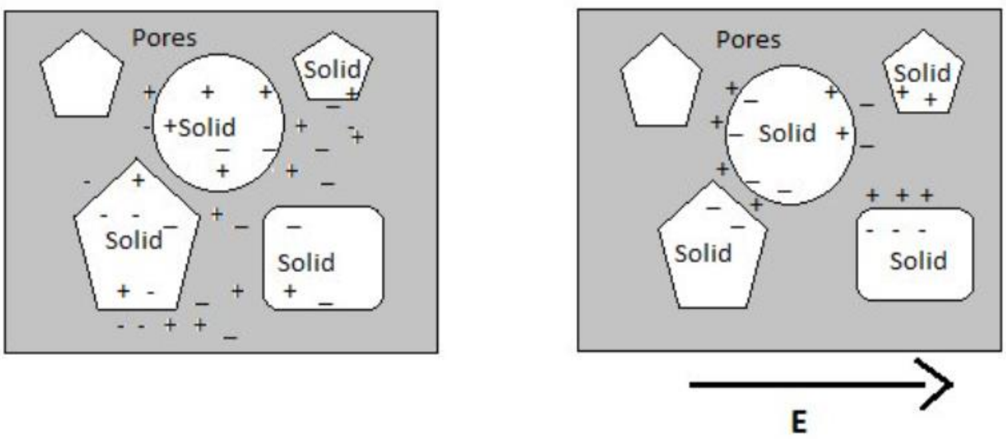

Fig. 1.7 Interfacial polarization in a dielectric material [49].

1.4 Frequency dependent electric polarization

Frequency dependence feature of the dielectric properties and polarizability can be shown in the presence of various polarization mechanism. Interfacial polarization requires long time to respond which depends on the type of charge carriers and dielectric materials. Thus interfacial polarization is effective mainly at lower frequencies and it is not effective at higher frequencies because charge carriers cannot respond electric field variation in short range of time. Other polarization mechanism like electronic, ionic and orientational polarizations requires short range of time ($<10^{-5}$ s) to respond. Fig. 1.8 and Fig. 1.9 represents variation of dielectric properties and polarizability with frequency respectively.

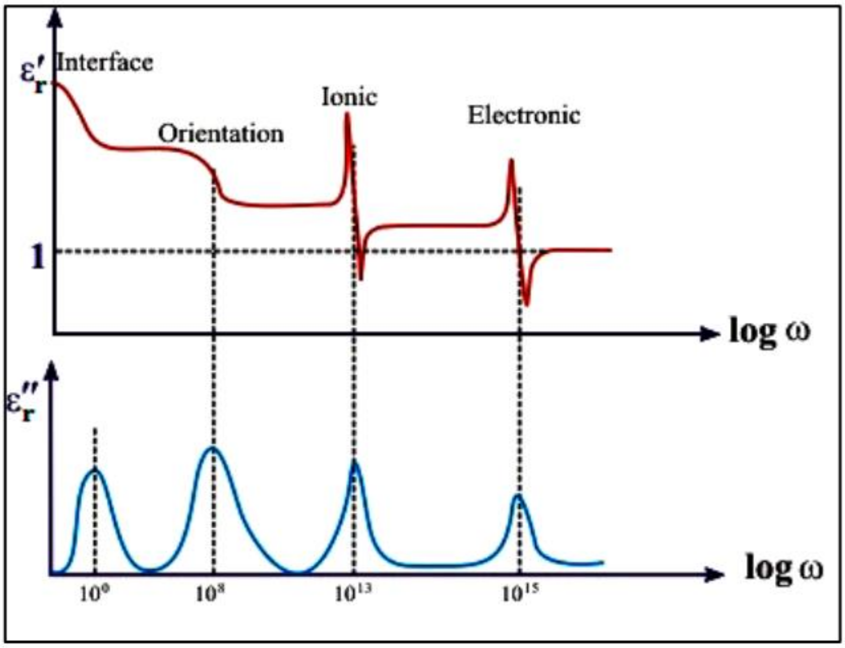

Fig. 1.8 Frequency dependence of permittivity due to various polarization [50].

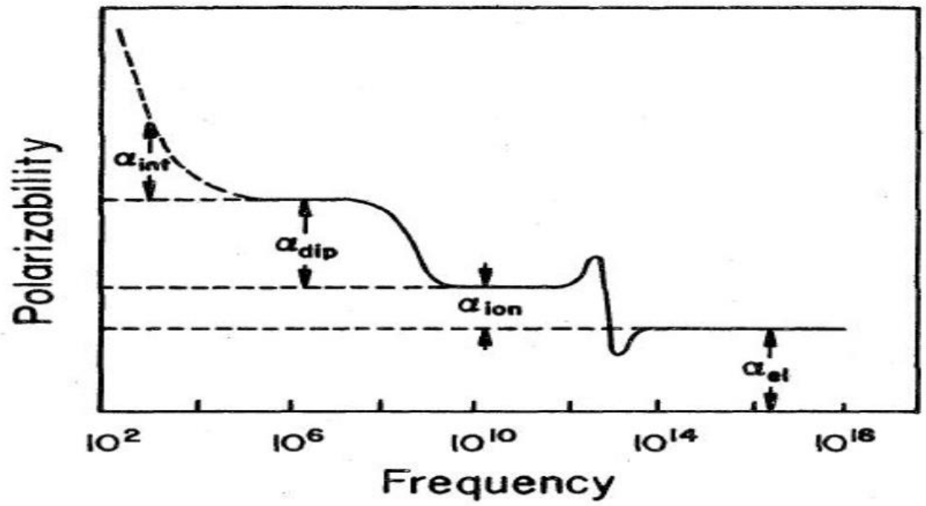

Fig.1.9 Frequency dependence of polarizability representing various contribution of various polarization mechanisms [51].

1.5 Different types of Energy storage dielectric materials

There are two major class of dielectrics namely linear and nonlinear dielectrics.

1.5.1 Linear Dielectrics

Linear dielectrics are characterized by dielectric materials where the induced polarization exhibits a direct proportionality to the electric field. The P-E curve illustrates a linear correlation between induced polarization and the applied electric field for linear dielectrics. Furthermore, these materials feature an energy storage density that is directly proportional to the square of the applied external electric field, as expressed by equation 1.2.

1.5.2 Nonlinear Dielectrics

Dielectric materials which have nonlinear relationship between E and P with hysteresis is known as nonlinear dielectrics. Nonlinear dielectrics represents large nonlinear dielectric constant and nonzero polarization even in the absence of externally applied electric field. Nonlinear dielectrics may express some special physical phenomena like piezoelectric effect, pyroelectric effect and spontaneous polarization. There are various types of nonlinear dielectrics which are discussed below:

- **Paraelectric Materials**

Paraelectric materials are characterized by the absence of dipoles in the absence of an external electric field. Upon the application of an external electric field, dipoles may emerge, resulting in weak polarization. This polarization is temporary and disappears once the applied electric field is removed.

- **Ferroelectric Materials**

Ferroelectricity is the property of some specific materials that are characterized by spontaneous polarization below ferroelectric curie temperature which can be reversed with the application of external electric field. The term ferroelectricity is analogous with ferromagnetism which have permanent magnetic dipole moment. The phenomena of ferroelectricity was first observed in 1920 in Rochelle salt by Joseph Valasek.

If there are two equal and opposite charges placed at a certain distance, it forms a electric dipole. The dipole moment of such dipole is given $\boldsymbol{\mu} = \mathbf{q} \times \mathbf{r}$ by equation 1.4.

A ferroelectric material possesses a permanent dipole moment resulting from the combined vector sum of dipole moments from all dipoles within a unit cell of its crystal structure.

This characteristic is absent in materials with crystal structures featuring a Center of Symmetry.

❖ Relaxor Ferroelectric Materials

Relaxor ferroelectrics, also known as relaxors, belong to the category of disordered ferroelectrics characterized by an undeveloped structure and properties. The disorder in the arrangement of different ions on the crystallographic sites is the basic feature of relaxors which is known as compositional disorder. Relaxor behaviour in perovskite structure is due to the existence of lattice disorder and polar nanoregions (PNR) at temperature sufficiently higher than melting temperature (Tm)[52]. Relaxor ferroelectric materials have high dielectric constants in comparison to conventional ferroelectric materials. Like normal ferroelectrcs, Relaxor ferroelectric materials represent permanent dipole moment. Relaxor ferroelectric domains are of nano length scale while normal ferroelectric domains are of micro length scale and require less energy to align in electric field direction [53]. Some basic features of relaxor ferroelectrics are as follows.

- In relaxor ferroelectrics there is no phase transition at Tm.
- Relaxors have broad ferroelectric transition and high dielectric constant.
- In the curve of dielectric constant vs temperature, relaxors have frequency dependent peak temperature. It shifts at higher temperature with increasing frequency.

❖ Antiferroelectric Materials

An antiferroelectric material have an ordered pattern of electric dipole moments with adjacent dipoles in antiparallel manner [54]. In an antiferroelectric material, net spontaneous polarization is zero because effect of adjacent dipoles cancle each other. In general, these materials have high dielectric constant and its antiferroelectric property vanish above curie point. Due to the absence of ferroelectric domains at low electric fields, antiferroelectric materials exhibit a low coercive field, minimal dielectric loss, low remanent polarization and high saturation polarization, which are favorable characteristics for applications in energy storage. Under sufficiently high electric fields, antiparallel domains align with the external electric field and undergo a transition to a ferroelectric phase, a phenomenon known as a first-order antiferroelectric-to-ferroelectric phase transition. The strength of the external electric field required for this phase transformation depends on external factors such as temperature and stress, as well as the material's composition. Consequently, antiferroelectric materials show the behavior of ferroelectric materials at high electric fields. This transformation is reversible, and reducing the electric field below a critical threshold leads the material to revert from its ferroelectric state back to its original antiferroelectric form. P-E characteristics of antiferroelectric ceramics shows double hysteresis loop. Typical P-E hysteresis curves of linear dielectrics and different nonlinear dielectrics like paraelectric, ferroelectric, antiferroelectric and relaxor ferroelectrics are shown in Fig. 1.10.

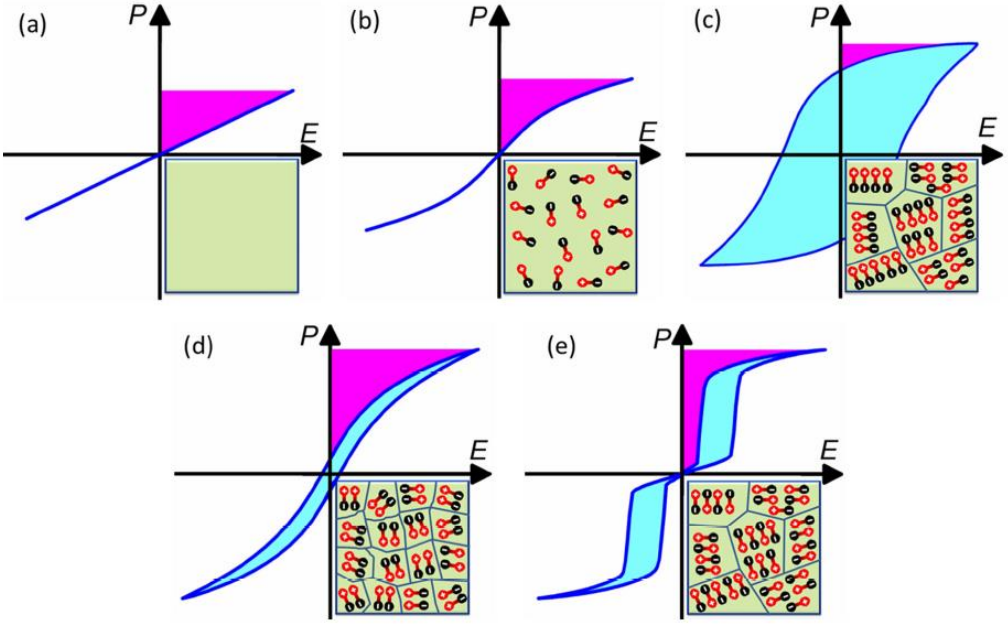

Fig. 1.10 P-E characteristics of (a) linear dielectrics, (b) paraelectric, (c) ferroelectric, (d) relaxor ferroelectric and (e) antiferroelectric materials [33].

- **Polymer based dielectrics**

Polymeric dielectrics that exhibit elevated dielectric breakdown strength, minimal dielectric loss, and a lightweight nature are the preferred option for energy storage applications. Dielectric materials with high energy storage density are essential to minimize the dimensions and weight of capacitors. Various linear polymer dielectrics like polyester, polypropylene, polycarbonate etc are used in the industry from more than half century. Recent study on aromatic polyurea has shown that polymer film can tolerate electric field upto 8000 kV/cm and recoverable energy density more than 12 J/cm^3 has been achieved at this electric field. The dielectric constant of aromatic polyurea is about 4 [23] . Thus major disadvantage of linear polymer dielectrics is its low dielectric constant on which energy storage density directly depends.

Nonlinear dielectrics have high dielectric constant and large polarization than that of linear dielectrics due to high dipole density. Ferroelectric polymers exhibit greater energy density compared to linear dielectrics. Among nonlinear dielectrics, polymers based on PVDF have been widely employed in energy storage applications due to their high dielectric constant and ease of large-scale processing. Therefore, nonlinear dielectric materials can serve as substitutes for linear dielectric materials in high-energy storage applications. Various methods have been proposed to improve the energy density of nonlinear polymer dielectric films which will be discussed later in section 1.9.

1.6 Ferroelectricity in PVDF polymer

Polyvinylidene difluoride is non-reactive thermoplastic fluoropolymer formed through polymerization of vinylidene difluoride. Polyvinylidene fluoride (PVDF) polymer is semicrystalline in nature and possess ferroelectric and piezoelectric properties [55]. PVDF has higher dielectric constant compared to other polymers and dielectric breakdown strength of up to 5000 kV/cm characterized by the chemical formula $[-CH2-CF2]_n$ [55] .

Hydrogen and fluorine have almost same atomic radius which facilitates the development of distinct crystal structure. It has four different crystalline phases: α, β, γ and δ with α being nonpolar while other phases are polar [56]. PVDF polymer has low density i.e. 1.78 g/cm^3 and low melting temperature at around 177 ^{0}C in comparison to other fluoropolymers. Its glass transition temperature (Tg) occurs around -35 ^{0}C and is around 60 % crystalline. PVDF is a ferroelectric polymer which exhibits pyroelectric and piezoelectric properties with negative d_{33} values when it is poled. β PVDF polymer has TTTT configuration in which H and F atom are on opposite side of main polymer chain and thus have non zero dipole moment and possess spontaneous polarization [57,58]. Normal processed PVDF is in α phase which is not piezoelectric in nature. Piezoelectric β phase can be obtained mainly by stretching or annealing process. Piezoelectric β phase of PVDF can also be obtained in thin film form because of high residual stress between thin film and substrate on which it has been deposited. Piezoelectric β, γ and δ phase of PVDF shows ferroelectric nature due to presence of net permanent dipole moment in unit cell of crystal structure of PVDF. Chemical structure of α, β and γ phase of PVDF is shown in Fig. 1.11.

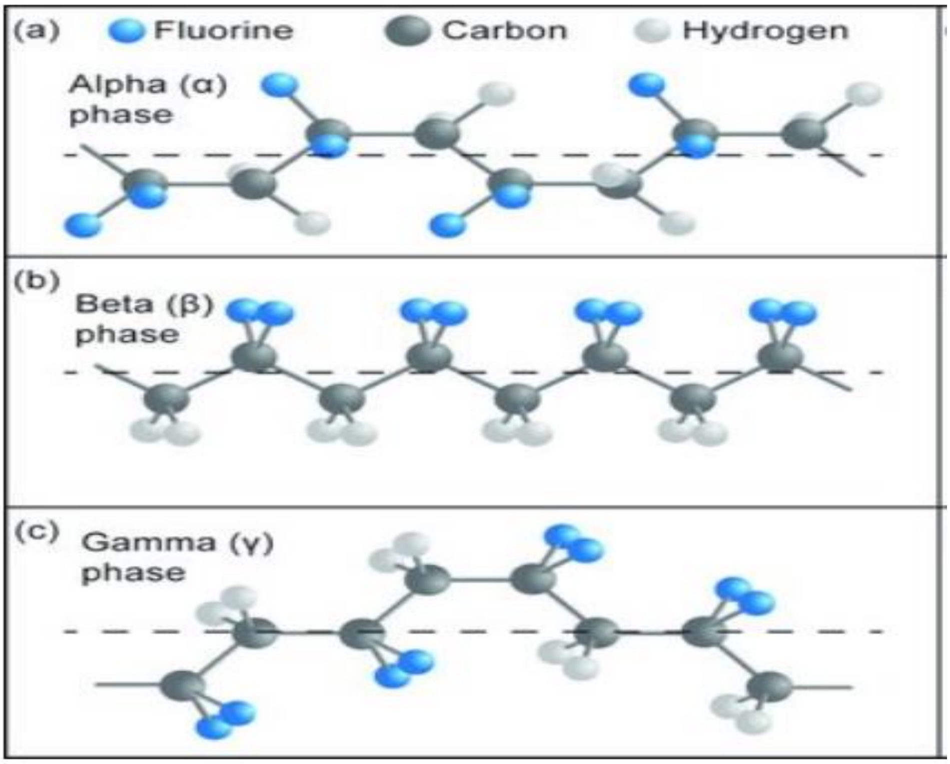

Fig. 1.11 Chemical structure of α, β and γ phase of PVDF [59].

1.7 Dielectric breakdown strength of dielectric material

The maximum applied external electric field that a dielectric material can sustain before undergoing electrical breakdown is known as dielectric breakdown strength [39,60]. Dielectric strength of a dielectric material depends upon the microstructural parameter like grain size and porosity [61]. There are mainly three mechanisms responsible for breakdown of the polymers namely electromechanical, thermal and fast avalanche breakdown. In fast avalanche breakdown, electrons are accelerated by the applied electric field which results in ionization of molecules during collision. Thus, regeneration of additional free electrons create an electron avalanche. At low temperature, fast avalanches dominate and at higher temperature, electromechanical breakdown dominates due to decrement in the mechanical properties of polymers at higher temperature. Thermal breakdown occurs generally with electromechanical breakdown or fast avalanche. The intrinsic breakdown strength of a dielectric material is defined as theoretical value of externally applied electric field to occur breakdown in perfect materials that have no defects or impurities. The experimental value of dielectric breakdown strength of a polymer is low in comparison to intrinsic breakdown strength because of the effect of polymer structure and different kind of additives. The dielectric breakdown strength of a material not only depends on dominating breakdown mechanism but also on other several factors such as defects and impurities in the material, thickness of the sample, morphology of sample and measuring conditions like surrounding medium, electrodes, AC, DC or impulse voltages applied on the material. Intrinsic breakdown strength of dielectric materials is defined as theoretical value of maximum operating electric field without fast avalanche breakdown in its perfect materials. The intrinsic breakdown strength is based on the fast avalanche mechanism and thus it depends only on the temperature and physical properties of the material. In Avalanche breakdown, electrons are accelerated by applied electric field which causes ionization of molecules during collision. Thus regeneration of extra electron happens and this process goes on if electrons gain sufficient kinetic energy which results in formation of conduction pathway throughout the dielectric material. These conduction paths are also created slowly even at lower applied voltages if it is applied for longer time and it is known as trees. There are mainly two categories of trees first one is water trees and second one is electrical trees. Electrical trees are caused by erosion due to discharges of gas and water trees are generated due to presence of water in the material. Water treeing is the degradation phenomena of polymers which happens if there is water present in the materials under high voltage conditions. Breakdown phenomena which happen due to electrical trees is known as erosion breakdown. In general, the creation and expansion of electrical trees in the dielectric materials is due to electronic avalanche mechanism which results in dielectric breakdown of the polymers. The electrical trees extend across the bottom and top electrodes and results in breakdown of materials which is generally due to structural flaws in the composite film. The distance between interaction of electrons and the polymer matrix is known as mean free path and electrons acquire kinetic energy while moving through path due to applied electric field. Breakdown mechanism basically depends upon mean free path of electrons and applied external electric field.

1.8 Methods for determination of energy storage density in dielectric capacitor

Let us consider a parallel plate capacitor which plate/electrode area is A and these electrodes are separated by a small distance d. If a dielectric material with dielectric constant ε_r is placed between the electrodes, then the capacitance of the parallel plate capacitor can be written as

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \qquad 1.14$$

From the above formula, it can be concluded that the capacitance of a parallel plate capacitor depends on the plate area, separation between plates and dielectric medium/material inserted between them. Thus we can conclude that we can insert a material of high dielectric constant between the parallel plates to increase the capacitance of the capacitor. When we apply electric potential between the electrodes, then the electrical energy is stored in the dielectric material in the form of electric field which can be determined by using formula

$$W = \int_0^Q V dq = \int_0^Q \frac{q}{C} dq = \frac{Q^2}{2C} = \frac{1}{2} CV^2 \qquad 1.15$$

Energy stored per unit volume of a dielectric material is known as energy storage density (U_e). The energy storage density of a dielectric material can be assessed through two distinct methods:

- **Static way**

In this method, first capacitor is fully charged by external source and electrical energy is stored in the dielectric material. Then, capacitor is discharged through load R. If transient current I is flowing through the closed circuit, then discharged energy can be calculated using below formula[62]

$$W = \int I^2 (t) R dt \qquad 1.16$$

Where t is the discharged time and R is the resistance of load through which capacitor has been discharged. Now, the recoverable energy storage density can be determined by the ratio of W with volume of the capacitor (Ad) which is given as

$$U_{rec} = \frac{W}{Ad} \qquad 1.17$$

- **Dynamic way**

We know that charge density (Q/A) on the conductor plates of a parallel plate capacitor is equivalent to electrical displacement ($D = \varepsilon_0 \varepsilon_r E$) of dielectric material placed in a capacitor. The energy storage density U_e can be determined from the following formula

$$U_e = \frac{W}{Ad} = \frac{\int_0^Q V dQ}{Ad} = \int_0^{D_m} E dD \qquad 1.18$$

Where $E = \frac{V}{d}$ is an applied external electric field. For a dielectric material with high dielectric permittivity, electrical displacement is nearly equal to electric polarization. Thus, electric displacement can be replaced by electric polarization in above equation. Thus equation becomes

$$U_e = \int_0^{P_m} E dP \qquad 1.19$$

From the above formula, we can see that energy storage density of a dielectric material can be qualitatively determined using numerical integration of P-E hysteresis curve which is equal to the area under the P-E curve and P axix. When a dielectric material is subjected to external electric field, polarization increases upto P_m with increasing electric field upto E_m and electrical energy is stored in the dielectric material. During the discharge process, electric field is decreased from E_m to zero, P-E curve follows different path and recoverable electrical energy is released. Recoverable energy has been shown by green area and dielectric loss is shown by red area in Fig. 1.12.

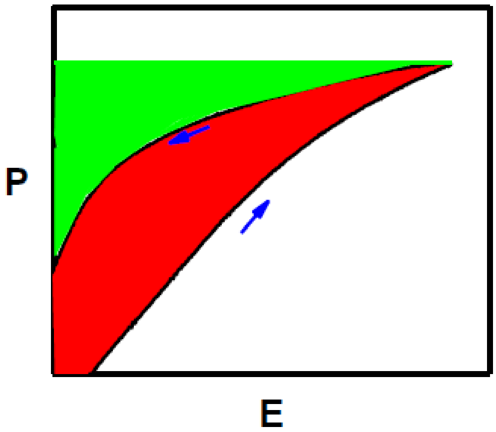

Fig. 1.12. Typical dependence of Polarization of Electric field for ferroelectrics in first quarter [39].

The energy discharge efficiency is determined using below formula

$$\eta = \frac{U_{rec}}{U_e} \times 100\ \% \qquad 1.20$$

And U_e can be written as[63]

$$U_e = \int_0^{P_m} E dP = \int_0^{E_m} \varepsilon_0\, \varepsilon_r E \mathrm{d}E = \frac{1}{2} \varepsilon_0 \varepsilon_r E_b^2 \qquad 1.21$$

Where ε_0 is the permittivity of free space and ε_r is the dielectric constant of the material.

A capacitor which is filled with linear dielectrics possess energy density given by above equation and as can be seen clearly that it is directly proportional to the square of applied external electric field of the capacitor. Thus, Enhancing the dielectric breakdown strength of a dielectric material contributes to an increased energy storage density. The crucial factors for achieving high energy storage density include a high breakdown strength (E_b) and large polarization. In general, if there is no conduction loss, there is no remanent polarization at E=0 and no coercive electric field at P = 0. In this case, maximum energy storage density can be obtained.

1.9 Interface effect in Polymer nanocomposites

The introduction of a nanomaterial into polymer matrix highly affects the properties of such formed dielectric nanocomposites. There are some important parameters like crystallinity, polymer chain mobility, coulombic potential, polymer chain conformation which affects the interaction of nanoparticles with polymer matrix [64,65]. The impact of interfaces in the polymer nanocomposites can be understood using two hypothetical models Lewis's model and Tanaka's model which has been discussed below [66,67].

- **Lewis's Model**

The reinforcement of nanofillers in the polymer matrix creates various interfaces of nanometer range. As we know that there is a difference in the chemical potential or fermi level of nanofiller and polymer matrix, so the surface of nanofillers get charged. As a respond, development of counter charge happens near the nanofiller surface [68]. Let us consider a positive charge developed inside the polymer matrix as shown in Fig. 1.13 which shows variation of electrical potential distribution Ψ(r) relative to distance from nanofiller surface. Here, for simplicity we have considered the surface of nanofillers as plane surface. Coulombic interaction takes place between charged nanofiller and positively developed charge in polymer matrix, hence redistribution of charges happen in polymer matrix which creates an electrical double layer. Electrical double layer is made up of Gouy-chapman diffuse layer and stern layer [68]. The stern layer is developed on the nanofiller surface because of adsorption of ions. Around the stern layer, there is formation of diffused layer with the distribution of negative and positive ions. The dielectric properties of the polymer nanocomposites are determined by the diffused layer.

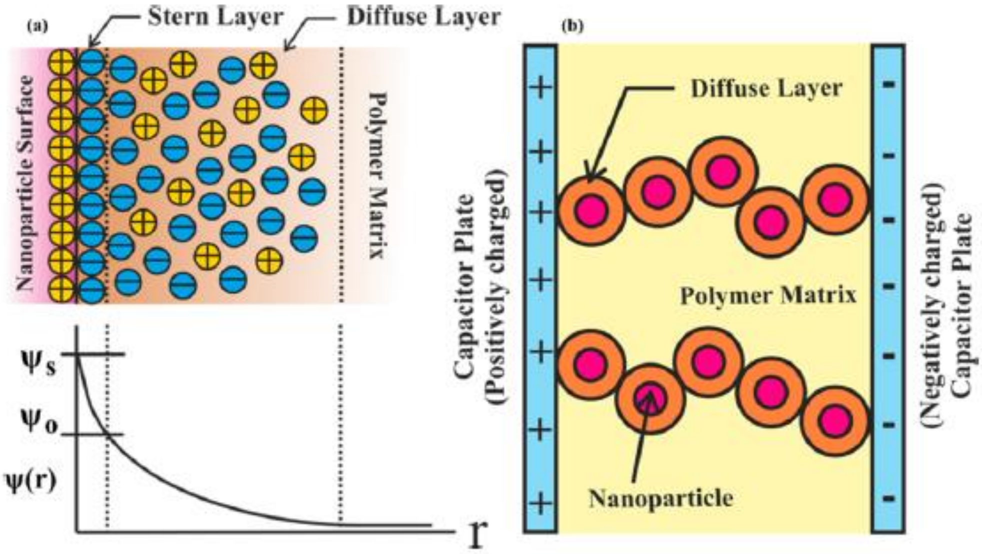

Fig. 1.13 (a) The polymer matrix with mobile ions, generating a diffuse electrical double layer due to the presence of positively charged particles, resulting electrical potential distribution Ψ(r), (b) Conduction within the composite through the diffuse double layer[2].

- **Tanaka’s Model**

Tanaka model is a multicore model to explain interfacial interaction when the spherical nanofillers are reinforced in the polymer matrix [69]. In this model, interface layer has been divided into three layers namely bonded layer, bound layer and loose layer and can be seen in Fig. 1.14 The bonded layer is the nearest layer from the nanofiller which is strongly bonded to nanofiller and polymer matrix both with thickness of about 1 nm [69]. This strong bonding is due to either vander waals force, covalent, ionic or hydrogen bonding. The second layer is known as bound layer and it is of around 2-10 nm thickness that depends on the interaction between nanofiller and polymer matrix. In the bound layer, the interaction of polymer chain with bonded layer and surface of nanofiller happens and polymer chains are strongly bound. The third layer is known as loose layer and it is loosely bound with bound layer with the thickness of several 10 nm order. In this region, polymer matrix shows different mobility, free volume, crystallinity and chain conformation than that of bulk polymer matrix [70,71]. The orientation of dipoles is affected in bound layer and reduction of free volume takes place in loose layer. Thus, decrement in the value of dielectric constant takes place and selection of suitable coupling agent plays very important role to achieve high energy storage density.

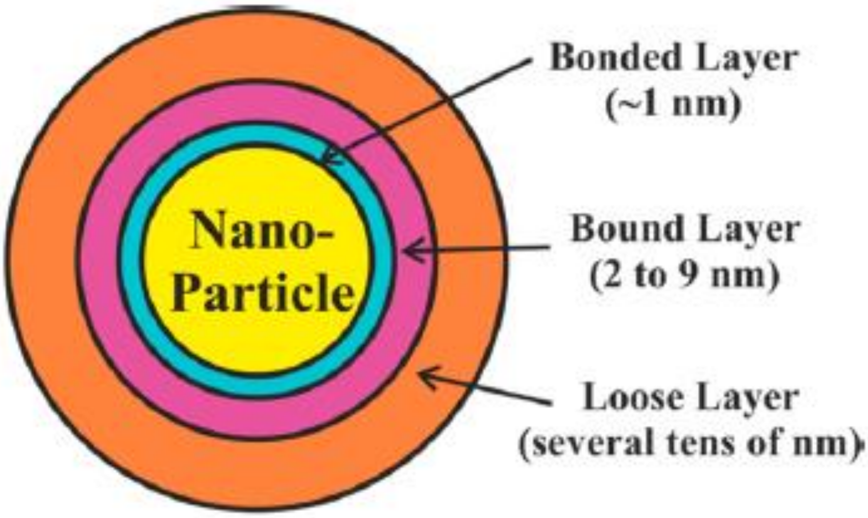

Fig. 1.14 Representation of Tanaka's model for nanoparticle-polymer interfaces [2].

1.10 Methods to improve the energy storage property of nonlinear dielectric polymers

As we are aware, the energy storage density of nonlinear dielectric materials is directly influenced by factors such as maximum polarization, breakdown strength, and remanent polarization. Therefore, enhancing the energy storage density of nonlinear dielectrics involves increasing maximum polarization, minimizing remanent polarization, and improving the dielectric breakdown strength of the materials. Researchers have employed various synthesis techniques and some significant methods are explained below:

1.10.1 Modification of defects

As synthesized PVDF films have some defects, so these defects can be modified to get desired properties. It has been reported that ferroelectric PVDF polymers can be transformed into relaxor ferroelectrics with smaller crystalline size and very small remanent polarization using defect modification with irradiation process [27,43]. Remanent polarization of PVDF based polymers has been reduced using proton irradiation process [72–74]. Ferroelectric polymers can also be transformed into relaxor ferroelectrics using chemical modification. It has been reported that the addition of suitable amount of functional groups like chlorotrifluoroethylene (CTFE) and chlorofluoroethylene (CFE) into poly(vinylidenetrifluoroethylene) P(VDF-TrFE) polymer chain shows relatively high dielectric constant ~ 50 which is good sign for high energy storage applications [27,43]. The PVDF polymer-based copolymers like P(VDF-HFP) and P(VDF-CTFE) has been synthesized using chemical modification technique. In spite of having low dielectric constant, these copolymers have high energy storage density of around more than 20 J/cm^3 at much higher electric field 6000 kV/cm [44]. The dielectric breakdown strength of P(VDF-TrFE-CFE) has been reported upto 4000 kV/cm and at this electric field, discharge energy density has been obtained upto 9 J/cm^3 [18]. Defect modification process requires highly complicated irradiation process or chemical synthesis with precisely controlled polymer composition and reaction condition which enhances the cost of prepared materials and thus limits its application for industrial purpose [55]. This is the main drawback of defect modification process.

1.10.2 Blending polymers

A polymer blend is consist of two or more dissimilar polymers which have been blended each other to develop new material with improved physical properties in comparison to base polymers. This method is beneficial for enhancing the dielectric properties of nonlinear dielectric polymers . It has been observed that polymer blend exhibits larger maximum polarization and smaller remanent polarization in comparison to base polymers [75]. Previously, It has been reported that polymethylmethacrylate (PMMA) is miscible in P(VDF-TrFE-CFE) and P(VDF-HFP). Also, blending of PMMA with ferroelectric polymers has decreased the crystallinity, increased mechanical modulus and reduced polymer crystal size which provides sufficient space for dipoles to flip. Thus, there is reduction in the value of remanent polarization and dielectric loss of the obtained polymer blend [27].

Shezad et al has reported the improved dielectric and ferroelectric properties of blends of P(VDF-CTFE) copolymer and P(VDF-TrFE-CFE) terpolymer. Blending of small proportion of copolymer with terpolymer has increased breakdown strength and polarization properties due to increased elastic modulus and interfacial effect at the interface of polymers respectively [76]. A lot of recent research suggest that blending is an easy and inexpensive way to improve the dielectric properties of nonlinear polymer dielectrics and make it more suitable for energy storage applications. However, miscibility of the polymer plays major role that affects the homogeneity of the polymer blends.

1.10.3 Grafting Polymers

Grafting is a process in which nanomers are covalently bonded onto the polymer chain. Graft copolymer is a class of branched copolymer in which structure of the side chain is different than that of the main chain of copolymer. The side chains may be homopolymer or different copolymer. The grafting of the polymers is a very attractive technique to admit different functional groups to the main side of the polymer for improving the structural and electrical properties. Various other properties such as melting temperature, crystallinity, adhesion, hydrophobicity and hydrophilicity can also be changed using graft copolymerization technique [77,78]. Researchers has grafted the ferroelectric PVDF polymer using polystyrene with the help of electron beam induced graft copolymerization and improved dielectric constant and dielectric breakdown strength of grafted copolymer has been obtained around 90 and 4000 kV/cm respectively which is higher in comparison to pure PVDF polymer [79]. In another research, PVDF has been grafted with HEMA (2-hydroxyyethylmethacrylate) using above mentioned technique and enhanced dielectric constant ~ 47 has been achieved. The various studies on grafting polymers have suggested that graft copolymerization using a suitable base polymer is a recommended technique to improve the dielectric and energy storage properties. Blending and grafting process of polymers is shown in Fig.1.15.

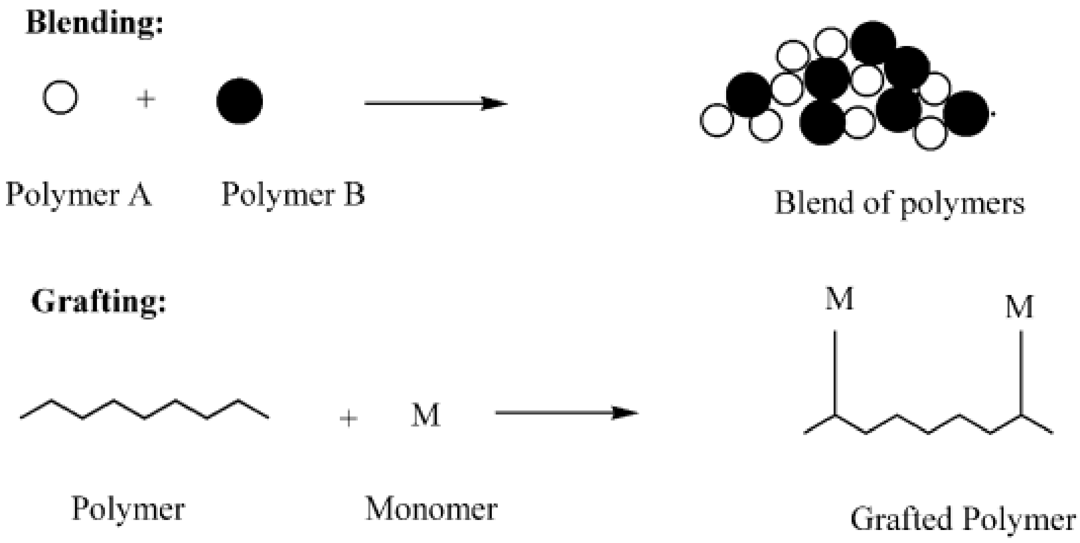

Fig. 1.15 Representation of Blending and grafting process[80].

1.10.4 Polymer based nanocomposites

In general, ceramics have high dielectric constant and low dielectric breakdown strength which lowers the energy storage density of dielectric capacitors. It is very difficult to synthesize multilayer ceramic capacitors that have high capacitance due to inflexible nature of ceramics. On other hand, polymers have low dielectric constant and large dielectric breakdown strength which also decreases the energy storage density in polymeric capacitors. Polymers can be easily processed into different shape and size. Composite materials that are made up of ceramics and polymers have the properties of high dielectric constant of ceramics, large dielectric breakdown strength of polymers and easily synthesis process of polymers to form dielectric capacitors with reduced weight and large energy storage density [17]. PVDF polymer have highest dielectric constant around ~ 10 among all known polymers. Here, we will discuss synthesis route and electrical properties of PVDF based nanocomposites with different conducting and nonconducting type of fillers. It has been observed that the interface effect between filler and matrix plays significant role for enhancment of dielectric properties of nanocomposites in comparison to micro-sized composites [81]**.** The synthesis of polymer-based nanocomposites is still challenging because of certain limitations like particle agglomeration, nonuniform dispersion of particles, high local fields, dielectric loss, leakage currents. In order to decrease particle agglomeration and to improve the dispersion of particles, surface modification technique has been applied [82]. Covalent grafting of surface modified nanoparticles to the main polymer chain of PVDF polymer can improve the dispersion of nanoparticles in the polymer matrix [83]. Although, above studies represent remarkable progress in polymer nanocomposites, there are still plenty of rooms for further improvement. The major challenge in the area of polymer nanocomposites is that to improve the dielectric constant, dielectric breakdown strength and reduce the dielectric loss simultaneously [18].

1.10.4.1 Polymer based nanocomposites with conducting nanofiller

In percolative systems, conductive particles are separated by thin dielectric polymer layers, creating a heterogeneous system that can function as a dielectric with exceptional energy storage characteristics [84]. The effective dielectric permittivity of these composites is described by a classic explicit law which depend on matrix permittivity, percolation threshold and dielectric critical exponent which is nearly equal to 1, different from the linear rule of mixtures [14]. The dielectric permittivity's critical behaviour near the percolation threshold can be understood using the micro capacitor model [85]. According to this model, adjacent conductive particles form local capacitors, with the fillers acting as electrodes and a thin host polymer layer serving as the dielectric. As the filler content increases, the network of local capacitors expands between two virtual electrodes, each contributing significantly to a large capacitance. This enhanced capacitance is associated with a notable rise in the local electric field when conductive fillers are in close proximity near the percolation threshold. This increased local electric field facilitates the movement and buildup of charge carriers at the interface between filler and matrix. These charge carriers produced via surface plasma resonance or external electrode-induced charge injection depend on the relaxation times of the two phases. The consequential interfacial polarization identified as the Maxwell-Wagner-Sillars (MWS) effect is responsible for a significant rise in permittivity at lower frequencies[85]. To attain a high permittivity, ensuring a low percolation threshold in percolative composites with conductive fillers is crucial. This characteristic not only enables exceptional mechanical flexibility but also results in reduced volume and weight. Consequently, the effective dielectric permittivity of a percolative nanocomposite shows an inverse relationship with the gap between the percolation threshold and the actual volume fraction of fillers. Therefore, achieving high dielectric permittivity is possible only when the filler loading is very close to or less than the percolation threshold. By maintaining a proper proportion of filler loading, percolative composites can manifest high dielectric permittivity. Various percolative polymer composites have exhibited elevated permittivity values, spanning from hundreds to thousands. These composites integrate a variety of conductive and semiconducting particles including metal particles, carbon nanofibers, carbon nanotubes (CNTs), graphene, and ZnO [3–6,86].

Dang et al. initially introduced and explained a percolative Ni/PVDF composite designed for energy storage applications [87]. The dielectric permittivity of these composites has been reported as ~ 400 at 17 vol% of Ni nearly at percolation threshold. Compared to spherical conductive particles, one-dimensional carbon materials with significant aspect ratios can achieve considerably lower percolation threshold. The increment in the value of dielectric permittivity ~ 600 was reported near 8 vol% percolation threshold in surface modified multiwall carbon nanotube (MWNT) using 3,4,5-trifluorobromobenzene (TFBB)/PVDF nanocomposites [88]. This high dielectric permittivity was due to MWS effect at the percolation threshold and thin insulating layer of PVDF surrounding the functionalized MWNT. An alternative approach for developing high permittivity percolative composites involves two-dimensional conductive fillers that have a disc or plate-like shape. This design was employed by He and his colleagues who created a polymer nanocomposite by aligning graphite nanoplates with their faces parallel to each other [5]. These nanoplates were separated by a thin layer of host polymer, resulting in the formation of numerous micro capacitors. Consequently, they achieved a significant dielectric permittivity of 2700 when the percolation threshold was as low as 1.0 vol%. The substantial variations in dielectric permittivity observed across various systems can be primarily attributed to factors such as the size, shape, and spatial arrangement of nanoparticles, as well as the inherent characteristics of polymer matrices and nanofillers[89].

Similarly, Dang et al. tried to modify the dielectric characteristics of nanocomposites consisting of Li-doped NiO (LNO) and polyvinylidene fluoride (PVDF) around the percolation threshold. They achieved this by finely tuning the conductivity of the nanofiller itself[90]. Their findings indicated that the percolation threshold rose with a decrease in the conductivity of LNO nanofillers. It is important to highlight that, in contrast to the additive properties, the dielectric response of composites is directly influenced by the polymer matrix. Consequently, polymer matrices with high permittivity are favored for the formation of percolative composites.

Despite achieving favorable dielectric permittivity and a low percolation threshold, polymer nanocomposites with conductive fillers still face challenges such as high dielectric loss, low dielectric strength, and a limited processing window which significantly hinder their practical applications in high-energy storage systems. The incorporation of conductive fillers increases dielectric permittivity in nanocomposites through mechanism like MWS polarization or micro capacitor effect. However, it also leads to elevated dielectric loss and leakage current within the conductive particle network formed near the critical percolation threshold, resulting in a substantial reduction in breakdown strength [7,91]. This phenomenon is commonly explained by the formation of micro-capacitors, causing an unusually large local electric field in the pure polymer region due to the close proximity of neighboring nanoparticles. The thin polymer layer between adjacent particles is unable to withstand the increasing local electric field, leading to a short circuit and inducing a significant leakage current[7]. The primary mechanism for electric conduction in percolative composites is recognized as tunneling, and according to the tunneling model, the interparticle tunneling conductivity (σ_{tun}) can be expressed as follows:[92]

$$\sigma_{tun} = A\exp\left(-\frac{l-2b}{d}\right) \tag{1.22}$$

where A is proportionality constant, l is inter particle distance, b is radius of particles and d is tunneling range. According to this model's description, the conductivity of nanocomposites exhibits exponential growth as the loading level tends the percolation threshold. This phenomenon occurs because the characteristic length (l) decreases rapidly with increasing loading, as determined through geometric calculations. However, these materials are unsuitable for use in capacitor dielectrics due to their lack of insulating properties. The considerable reduction in dielectric breakdown strength has a negative impact on the energy density of composites, due its quadratic correlation with electrostatic energy storage.

In recent years, various strategies have been developed to minimize direct contact between conductive particles close to percolation threshold, aiming to reduce dielectric loss, maximize dielectric breakdown strength and broaden the compositional range. A simple method involves introducing a barrier layer between particles in percolative nanocomposites to suppress tunneling current between adjacent conductive nanoparticles, resulting in significantly lower dielectric loss and increased breakdown strength. Moreover, the interfacial layers help to control the precise micro-capacitor structures near percolation threshold usually leading to a substantially broader compositional range for percolative composites. By carefully adjusting the properties of these barrier layers, percolative composites can achieve a desirable energy density due to increased permittivity and slightly reduced dielectric breakdown strength.

Wong and colleagues first introduced an interfacial layer in a metal polymer composite [93]. They coated 100 nm Al fillers with a thin layer (~ 3 nm) of Al_2O_3 then combined them with epoxy to fabricate percolative composites. The introduction of these core-shell particles in an epoxy polymer matrix led to a significant increase in dielectric permittivity without substantially impacting the matrix's inherent dielectric loss tangent. A high dielectric permittivity of up to 60 was reported at 50 wt% filler with a loss tangent of ~ 0.02. The Al_2O_3 interfacial layer effectively limits electron transfer between adjacent Al nanoparticles and maintains the loss tangent very low [93]. Beyond a filler loading of 50 wt%, a slight reduction in dielectric permittivity occurred due to the development of voids at higher filler concentrations, attributed to the existence of fractal clusters.

Compared to use a self-passivated inorganic shell, applying organic interfacial layers to conductive nanoparticles has proven to be a more versatile approach, offering greater flexibility in adjusting the dielectric properties of percolative composites. Qi et al. demonstrated this by modifying 40 nm Ag nanoparticles with a slender coating of mercaptosuccinic acid (MSA) molecules and then incorporating them into epoxy through an in-situ polymerization process [94]. As a result, the dielectric permittivity of the composites increased upto 300 with low loss tangent of < 0.05. The presence of organic coating makes it challenging to form a conductive filler network, significantly reducing dielectric loss and enabling a high concentration tolerance for high dielectric permittivity. These high permittivity and low loss tangent values hold promise for energy storage applications. However, as the Ag volume increases, the breakdown strength decreases significantly. This suggests that the organic surfactant coating fails to stop tunneling current at high fields because of loose morphology and structural defects. This substantial decline in dielectric breakdown strength results in a significant decrease in the energy density of the composites compared to the original polymer matrix, despite a slight increase as the percolation threshold is approached. Consequently, a denser organic layer with a robust structural integrity is necessary to improve both low-field and high-field dielectric properties, consequently boosting the energy density of percolative composites.

Shen and Nan recently addressed this challenge in Ag/epoxy percolative composites [95]. They initially coated Ag nanoparticles with carbonaceous organic shells using a one-pot hydrothermal method. These Ag@C core-shell nanoparticles were then blended with an epoxy matrix to fabricate percolative nanocomposites. These core-shell nanoparticles form a network near the percolation threshold, connecting the top and bottom electrodes on the sample. Each pair of neighboring particles acts as nanocapacitors, preventing direct contact between the Ag cores even at high filler loading of 30 vol%. Ag@C/epoxy nanocomposites exhibit high dielectric permittivity (~ 450) and extremely low dielectric loss (tan $\delta < 0.05$), with permittivity remaining stable even at high applied electric fields. However, the breakdown voltage decreases as the filler concentration increases. The energy storage density of the polymer matrix can be enhanced at certain optimal nanofiller loading with this improvement becoming more significant as the shell thickness increases. These optimal loadings are well below the percolation threshold which suggests that the high permittivity typically observed near the percolation threshold in most percolative systems may not translate into high energy density at high fields, although the low-field characteristics of composites are instructive.

1.10.4.2 Polymer based nanocomposites with nonconducting filler

Various studies have been performed to enhance the dielectric properties of composites for capacitive energy storage applications. Various perovskite ceramics such as $BaTiO_3$ (BT), $SrTiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$ (PZT) etc are extensively used as fillers in polymer nanocomposites due to their high dielectric constant. In ceramic polymer composites, main target is to disperse the ceramics of high dielectric constant into the polymer matrix to create large interfacial area in the composites which results in large permittivity of composites due to interfacial polarization. The dielectric and energy storage properties of various reported PVDF polymer-based nanocomposites with $BaTiO_3$ based perovskite fillers are discussed here.

Among various perovskite ceramics, BT is one of the most attentive filler due to its high dielectric permittivity which is around 2000, environmental friendly nature and commercial availability. Cherqaoui et al. have first dispersed BT nanoparticles in PVDF polymer matrix and studied above synthesized polymer ceramic composites [96]. Murlidhar et al. have also studied dielectric properties of BT/PVDF composites with the variation of frequency and weight fraction of BT nanoparticles. The permittivity value of BT/PVDF composites with 70 wt. % of BT nanoparticles was reported as 133 at 10 Hz frequency and room temperature [97]. Hao et al. has reported that BT nanoparticles with less than 10 nm diameter can enhance electric polarization and dielectric breakdown strength of the composite simultaneously because of larger interfacial area than that of conventional nanofillers [98]. In general, smaller size of nanofillers plays very crucial role for thin film composites because dielectrics in thin film form represents higher capacitance per unit volume. Dang et al. has also studied the dielectric properties of BT/PVDF composites at different frequencies with the variation of BT nanofiller size. They have reported significantly enhanced dielectric constant in case of BT/PVDF composites at lower frequency with nanosized BT filler due to large interface area and dipolar polarization as can be seen in Fig. 1.16 [99]. The nanosized filler at higher volume fraction cause aggregation and inhomogeneous distribution in polymer matrix due to high surface energy which results in lower dielectric constant and dielectric breakdown strength of the composites.

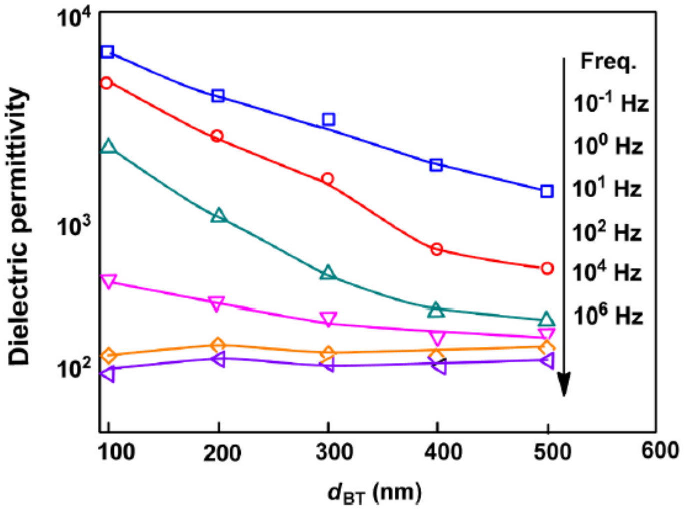

Fig. 1.16 Variation of dielectric permittivity of BT/PVDF composites with BT particle size at different frequencies [99].

Kim et al. modified the surface of Barium titanate nanoparticles using pentafluorobenzyl phosphonic acid (PFBPA) as coupling agent to get uniform distribution of nanoparticles in the polymer matrix and reduced the effect of aggregation [100]. The energy storage density in case of PFBPA-BT/poly(vinylidene fluoride -hexafluoropropylene) composites has been reported as 3.2 J/cm^3 at 50 volume fraction of nanofillers.

Yu Chen Lu et al. have synthesized BSYT/PVDF composite and reported the value of dielectric constant ~ 12 with 8.9 vol. % of BSYT at 100 Hz frequency which is greater than that of dielectric constant of pure PVDF [101] and can be seen in Fig. 1.17(a). Qingguo Chi et al. have found dielectric constants of ~18 and ~23 at 100 Hz frequency in case of PVDF/BT composites with 7 vol. % of BT nanofillers and PVDF/BZT-BCT composites respectively [102] as can be seen in Fig. 1.17(b). The BZT-BCT is a ceramic material which have large piezoelectric coefficient of 620 pC/N and high dielectric constant of 3370 at 1kHz frequency at room temperature. The dielectric constant of BZT-BCT/PVDF nanocomposite film is higher in comparison to BT/PVDF nanocomposites at same filler loading. The relaxation peaks corresponding to interfacial polarization in case of nanocomposites becomes broader and shifts toward higher frequency with increasing filler content which shows that addition of BZT-BCT nanofillers into composites enhances interfacial polarization.

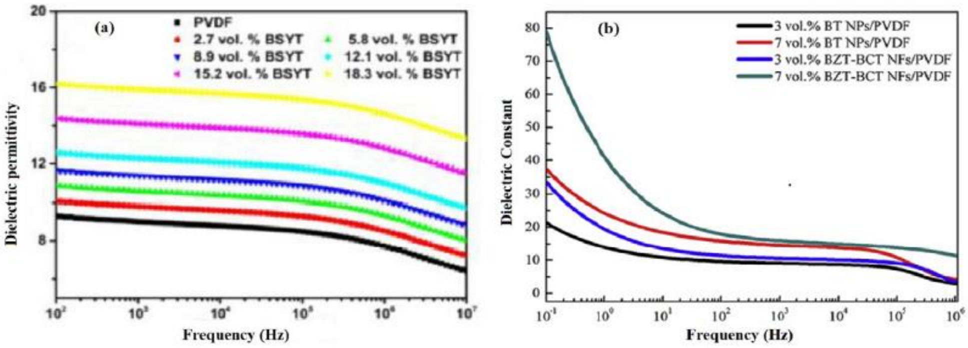

Fig. 1.17 Variation of permittivity with frequency at different nanofiller loading (a) BSYT/PVDF, (b) PVDF/BT NPs [102].

Li Wang et al. have reported the dielectric constant of $Ba_{0.6}Sr_{0.4}TiO_3$ (BST4)/PVDF composite with 40 vol. % of BST4 from 33.5 to 53.9 at 1 kHz frequency with variation of hot-pressing temperature upto 140 °C from room temperature [103]. There is less defects and better interface connectivity between PVDF polymer and BST4 fillers at higher pressing temperature which confirms that hot pressing temperature improves interface connectivity. There is decrement in the value of dielectric constant of composites with increasing frequency because of dipole orientation relaxation and interface polarization. Li wang et al. have synthesized BST/PVDF composites with 40 vol. % of surface modified BST filler using KH550 and reported the dielectric constant of above synthesized composites ~30 at 1kHz frequency [104]. The dielectric constant increases and decreases with increasing vol. % of BST and frequency at room temperature due to generation of polarization relaxation and dipole orientation relaxation within composites.

Xu Lu et al. have synthesized $BaTiO_3$/P(VDF-CTFE) nanocomposites using 40 vol. % of $BaTiO_3$ and found dielectric constant of nanocomposite ~53 at 100 Hz frequency [105]. Another group of Xu Lu et al. have synthesized $Ba_{0.5}Sr_{0.5}TiO_3$ (BST5)/P(VDF-CTFE) nanocomposites using 40 vol. % of BST5 and reported dielectric constant of nanocomposite as ~38 at 100 Hz frequency [106]. As can be seen from Fig. 1.18(a), the dielectric constant of BST5/P(VDF-CTFE) nanocomposite decreases with increasing frequency. The increment in the value of dielectric constant of nanocomposite was observed upto 40 vol. % of BST5 and after further increment in the vol. % of BST5, the decrement in the value of dielectric constant was observed due to the form and packing of ceramic nanofiller that affect the properties of nanocomposites as can be seen in Fig. 1.18(b). Further, upon increasing the volume fraction of nanofillers in the nanocomposites, nanofiller is unable to uniformly distribute within the polymer matrix which results in air voids, If we compare the above BT/P(VDF-CTFE) and BST5/P(VDF-CTFE) composites investigated by Xu Lu et al, better compatibility was observed in case of composites with BT in comparison to BST5. The dielectric permittivity in case of BT is greater than BST5. If vol. % of nanofillers are increased, dielectric constant of composite increases because of large permittivity of nanofillers and compositional alterations.

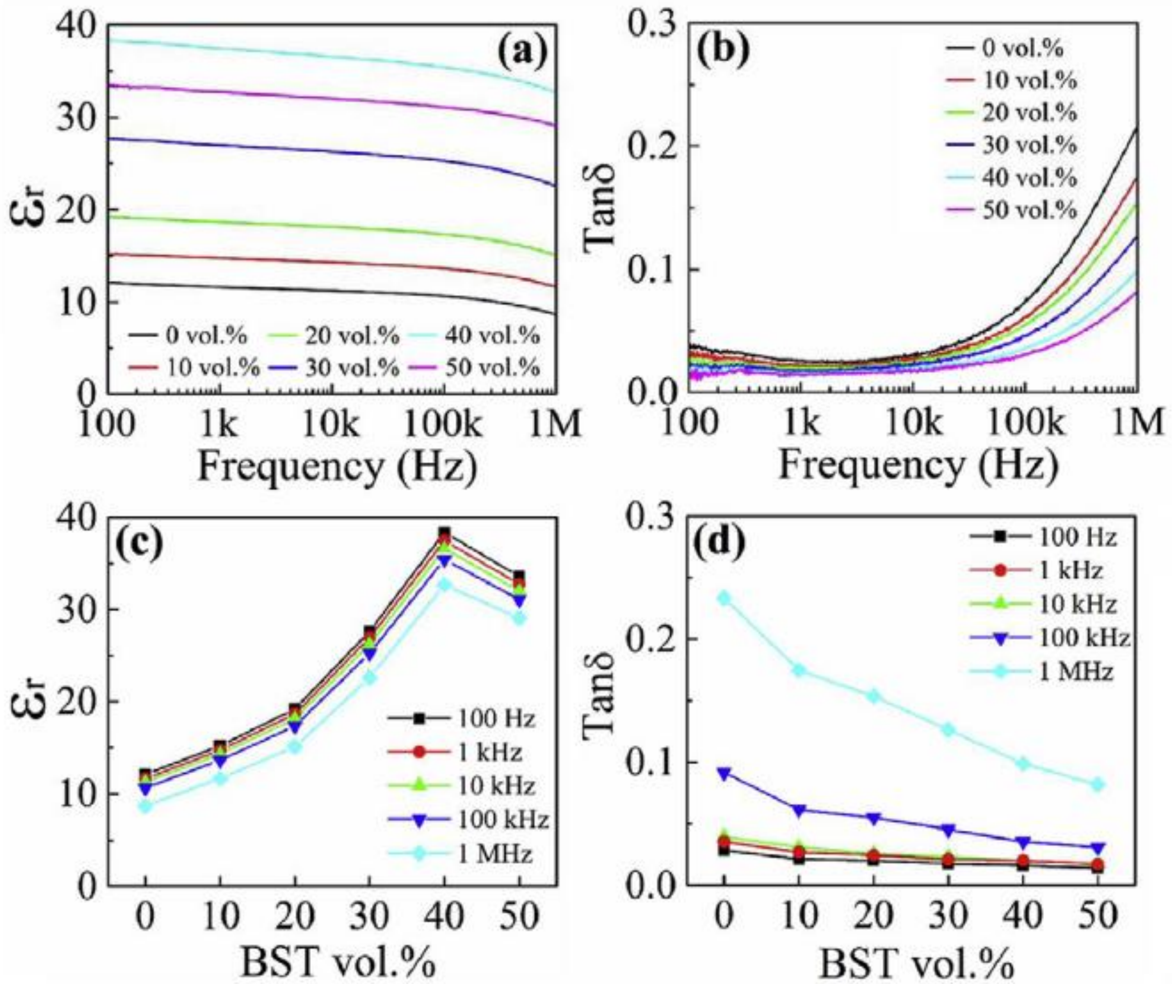

Fig. 1.18 (a) and (b) Variation of dielectric constant and dielectric loss with frequency in case of BST-VC$_{91}$ nanocomposite films, (c) and (d) dielectric constant and dielectric loss with BST filler variation[106].

Various PVDF based nanocomposites have been studied using ceramic nanoparticles reinforced in polymer matrix within percolation limit. Beyond percolation limit, dispersed ceramic nanoparticles forms interconnected conducting pathways in the composites. Deepankar Sri Gyan et al have synthesized PVDF/NaNbO$_3$ nanocomposites using NaNbO$_3$

ceramic as a matrix and PVDF polymer as a filler with the help of cold sintering process in order to partially rectify the percolation limit problem [107]. Theoretical value of dielectric breakdown strength and energy storage density has been obtained at room temperature ~ 1345 kV/cm and 6.1 J/cm^3 respectively at 80 wt. % of NaNbO3 and 20 wt. % of PVDF polymer. The discharged efficiency for NaNbO$_3$/PVDF annealed composite has been obtained ~ 64 % in present case. Thermally stable dielectric constant and dielectric loss with improved dielectric permittivity and reduced dielectric loss has been obtained in case of NaNbO$_3$/PVDF annealed composite which can be seen from Fig. 1.19.

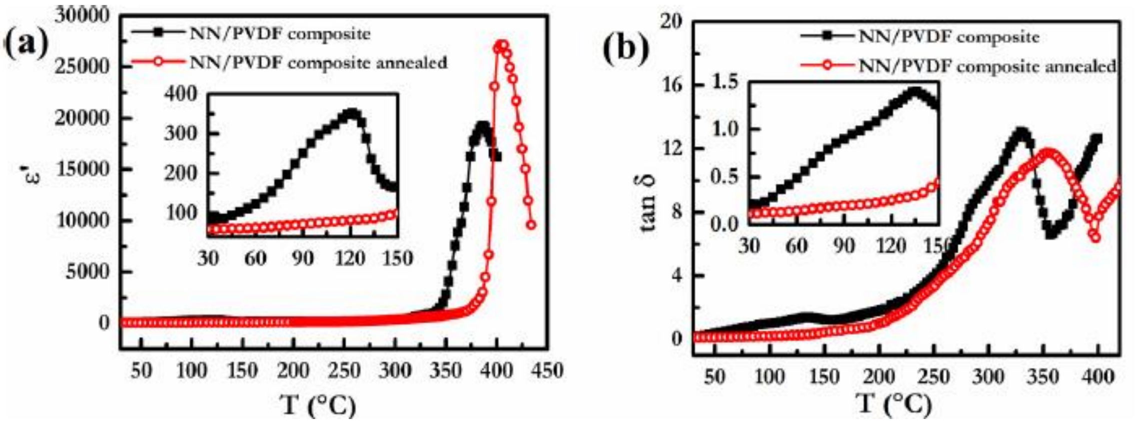

Fig. 1.19 (a) Dielectric constant and (b) dielectric loss of NaNbO$_3$/PVDF composite and NaNbO$_3$/PVDF annealed composite at 1KHz frequency [107].

1.11 Challenges in enhancing the energy storage capacity of polymer-ceramic nanocomposites

In general, the maximum energy density achievable in a nanocomposite material depends mainly on two key factors: the dielectric permittivity and the dielectric breakdown strength, which is the maximum applied external electric field material can withstand without short-circuiting. Therefore, the primary approach for increasing energy storage density is by enhancing the dielectric permittivity. Currently reported dielectric polymers, like polypropylene and epoxy resins, typically have dielectric permittivity values in the range of 2 to 5. However, much higher permittivity values can be attained with highly polarizable materials such as barium titanate ($BaTiO_3$) and polyvinylidene fluoride (PVDF) due to polarization generating from ion displacements and permanent dipole alignment, respectively [108]. We know that a material with a higher dielectric permittivity can store a proportionally greater amount of electrostatic energy. For example, PVDF based terpolymer P(VDF-TrFE-CFE) represents an impressive dielectric permittivity of up to 65 and have dielectric breakdown strength of order of 5000 KV/cm [109]. As a result, it works as an electrostatic capacitor with a remarkable recoverable energy density of 13 J/cm^3. In contrast, biaxially oriented polypropylene (BOPP) has a similar dielectric breakdown strength but a significantly lower maximum energy density of only 2 J/cm^3 due to its low dielectric permittivity (approximately 2.2) [110]. On the other hand, dielectric materials with ion displacements, such as ferroelectric $BaTiO_3$ or lead manganate niobate relaxors, possess very high dielectric permittivity ranging from hundreds to thousands [14,111]. However, they have lower dielectric breakdown strength compared to polymers and, as a result, can not fully utilize their higher polarizability to store high energy within the material.

One attractive approach involves blending of high dielectric breakdown strength polymers with metal oxides possessing a large dielectric permittivity. This is achieved by uniformly dispersing oxide nanoparticles within a polymer matrix [112]. In this manner, the nanoparticles contribute to an increase in the effective dielectric permittivity of the composite, as per effective medium theory, while the polymer matrices serve to safeguard against dielectric breakdown. Research in recent years has primarily focused on developing polymer nanocomposites and has achieved notable enhancements in their overall dielectric performance. This improvement has been accomplished using ferroelectric metal oxides like $BaTiO_3$, $CaCu_3Ti_4O_{12}$ (CCTO), and $Pb(Zr,Ti)O_3$ (PZT) [83,113]. Nevertheless, several persistent challenges remain from an energy-storage perspective.

One primary challenge pertains to the proper dispersion of oxide nanoparticles. The elevated surface energy of these nanoparticles often causes them to aggregate and undergo phase separation from the polymer matrix, especially when incorporated into an incompatible matrix. This results in the production of films with low quality and compromised dielectric properties, characterized by elevated dielectric loss and reduced dielectric strength [83].

One of the significant challenge faced by the polymer nanocomposite is to strategically optimize the concentration of particles to maximize their energy-storage capacity. To achieve a high effective permittivity and energy density, these materials typically require fillers with much higher permittivity than the surrounding polymer matrix. In such cases, the majority of the increase in effective dielectric permittivity comes from raising the average electric field within the polymer matrix, with only a minimal contribution from the high permittivity filler phase [111]. To attain a substantial increase in permittivity within the composite, a considerable amount of high permittivity nanoparticles is necessary. However, as the particle concentration increases, the dielectric strength sharply declines due to elevated defect density and percolation issues with low dielectric strength ceramic nanofillers [113]. The elevated proportion of fillers also results in a higher packing density of particles, which can create paths for breakdown through aggregated fillers. This leads to increased leakage current, reduced electric breakdown strength, and thus decrease in energy density [114]. Thus, in spite of improvement in the dielectric permittivity of polymer composites, the reduction in dielectric breakdown strength results in only a marginal enhancement in energy density compared to the pure polymer matrix. Consequently, it is crucial to determine the optimal volume fraction of nanoparticles in the nanocomposite to achieve both high energy density and a strong dielectric breakdown strength. This optimization ensures that capacitors made from films of this material can operate effectively at high voltages.

1.12 Effects of Surface Modification of Nanofillers in Polymer nanocomposites

Significant advancements have been made in the field of Ferroelectric Nanocomposite Dielectric Materials (FNDM) to enhance their energy-storage capacity by addressing some of the previously mentioned challenges. To illustrate, efforts have been made to enhance the compatibility between ceramic particles and polymer phases, thereby preventing issues like particle clustering, voids, and phase separation on a large scale. This is often achieved by using surfactants such as phosphate esters and oligomers, which enhance nanoparticle dispersion within the matrix and consequently improve the overall quality of the film [115]. However, one drawback is that the presence of residual free surfactants can lead to undesirable consequences, including deteriorated dielectric properties under applied fields, such as increased leakage current and elevated loss tangent. An alternative approach involves firmly bonding surface modifiers to nanoparticles through robust chemical bonds. This approach aims to significantly enhance compatibility between the filler and polymer matrix, ultimately improving the energy-storage performance of these nanocomposites [83,116]. For instance, Ramesh et al. employed trialkoxysilane surface modifiers to disperse $BaTiO_3$ nanoparticles within an epoxy polymer host [116]. Although the resulting composites exhibited a reasonably high permittivity value of up to 45, there was an unfortunate increase in the loss tangent compared to unmodified $BaTiO_3$ nanocomposites.

Surface modification of nanofillers by any means is famous technique to obtain nanocomposites with uniform distribution of nanofillers within threshold limit into polymer matrix. Peixuan Wu et al. have synthesized composites with 30 vol. % of surface modified BST5 filler using 15 wt. % silane coupling agent and P(VDF-CTFE) polymer matrix [117].

They have reported the dielectric constant of 95 at 100 Hz which is eight times greater than pure P(PVDF-CTFE) and three times greater than P(VDF-CTFE)/ BST5 composites (~31) with 30 vol. % of BST5 filler and without surface modification. The proper proportion of coupling agent for surface modification enhances the dielectric properties and beyond that conductivity increases. Dou Zhang et al. have synthesized TiO_2@PZT nanowire/ P(VDF-TrFE-CTFE) nanocomposites and obtained very high dielectric constant of 219 at 1 KHz in comparison to pure P(VDF-TrFE-CTFE) (~35) because of interfacial polarization [118].

Yanbin Shen et al. have reported dielectric constant of 14.5 at 1 KHz in case of BT@MEEAA (Methoxy ethoxy ethoxy acetic acid)/P(VDF-HFP) composites with 5 vol. % surface modified BT nanofillers which is greater than that of untreated 5 vol. % BT/P(VDF-HFP) composites (~13) and pure P(VDF-HFP) (~9) [119] which can be seen in Fig. 1.20(a)-(b). The value of dielectric constant decreases with increasing frequency because interfacial polarization dominates at lower frequency and at higher frequency, polarization of pure P(VDF-HFP) dipole becomes unable to respond the electric field.

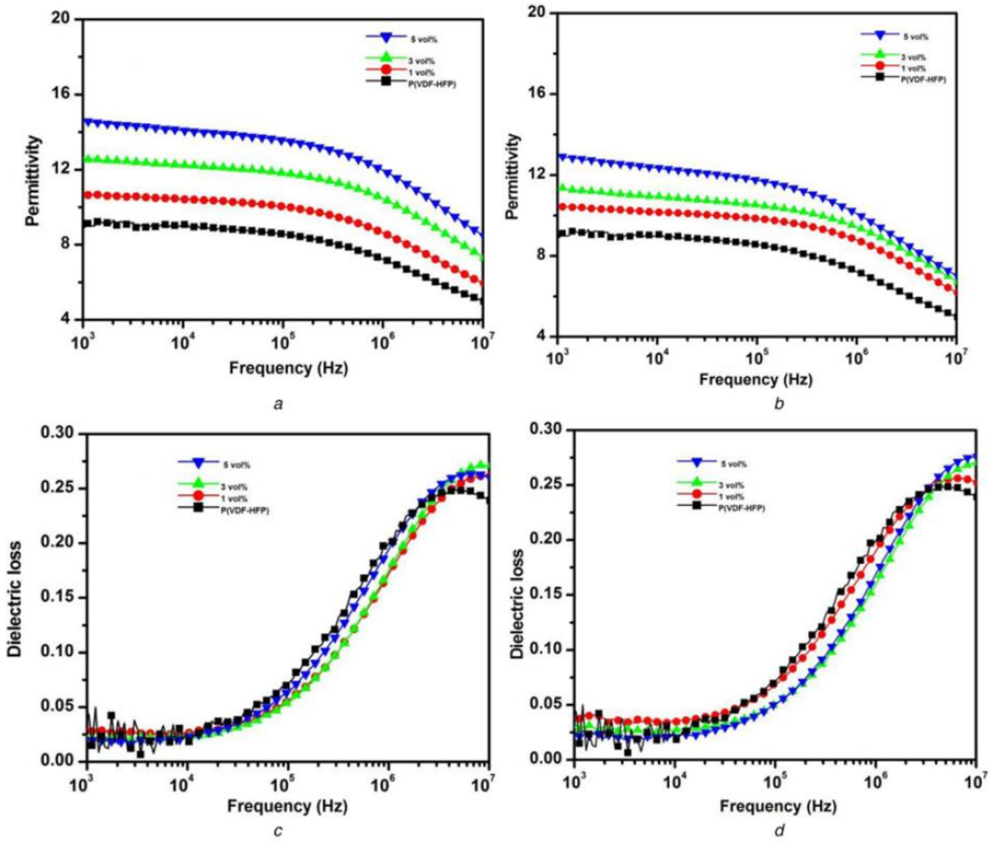

Fig. 1.20 Frequency dependent dielectric constant and dielectric loss of (a) and (c) P(VDF-HFP)/BT@MEEAA NPs, (b) and (d) P(VDF-HFP)/BT NPs [119].

Similarly, Kim and colleagues explained strong surface binding of $BaTiO_3$ nanoparticles using phosphonic acid [83]. They explored the use of above discussed specific surface functionality to regulate the interaction between $BaTiO_3$ and the polymer matrix, thereby promoting the formation of uniformly dispersed nanocomposites with high energy storage density. It is evident that the nanocomposites containing unmodified $BaTiO_3$ nanoparticles displayed significant aggregation and the presence of pinhole defects. In contrast, those incorporating modified $BaTiO_3$ nanoparticles exhibited relatively uniform films with consistent dispersion of nanoparticles in the polymer matrix. The nanocomposites containing 50 vol. % surface modified $BaTiO_3$ particles demonstrated a high permittivity (~37), low dielectric loss (less than 0.007), and a strong dielectric breakdown strength (over 2000 KV/cm). Consequently, the modified $BaTiO_3$ nanocomposites achieved a substantial calculated energy density of up to 6.1 J/cm³. Unlike Kim's surface modification approach, Wang et al. successfully fabricated nanosized surface modified $BaTiO_3$ using ethylene diamine in situ [120]. This surface modification significantly improved the dispersion of $BaTiO_3$ nanoparticles in organic solvents, resulting in the formation of uniform polymer nanocomposite films. The energy density of composites containing 23 vol. % modified BaTiO3 nearly doubled, increasing from 1.9 J/cm³ (for the neat polymer) to 3.7 J/cm³.

Zhou et al. employed hydrogen peroxide to surface hydroxylate $BaTiO_3$ nanoparticles and then blended with PVDF to fabricate polymer nanocomposites [121]. In the resulting composite, hydrogen bonds developed between the electrophilic atoms in PVDF and the -OH groups located on the surface of hydroxylated $BaTiO_3$ nanoparticles are depicted in Fig. 1.21(a). Compared to unmodified $BaTiO_3$ nanocomposites, the hydroxylated $BaTiO_3$ nanocomposites exhibited lower permittivity but significantly higher dielectric breakdown strength. Striking a balance between these characteristics led to the identification of a composite with 20 vol% hydroxylated $BaTiO_3$ particles, achieving a maximum energy density of 3.7 J/cm3 and a loss tangent of 0.02.

An alternative method for directly linking the polymer matrix to the nanoparticles involves the growth of the host polymer on the surface of nanofillers through an in situ synthesis technique. This approach has been extensively employed with various nanofillers like silica, nanotubes, and graphene oxide, and has proven effective in creating multi-core interfaces in dielectric nanocomposites [122]. For instance, Huang and Jiang successfully produced core-shell structured nanocomposites of $BaTiO_3$ and poly(methyl methacrylate) (PMMA) by using in situ atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) from the surface of $BaTiO_3$ nanoparticles [122]. This process is depicted schematically in Fig. 1.21(b).

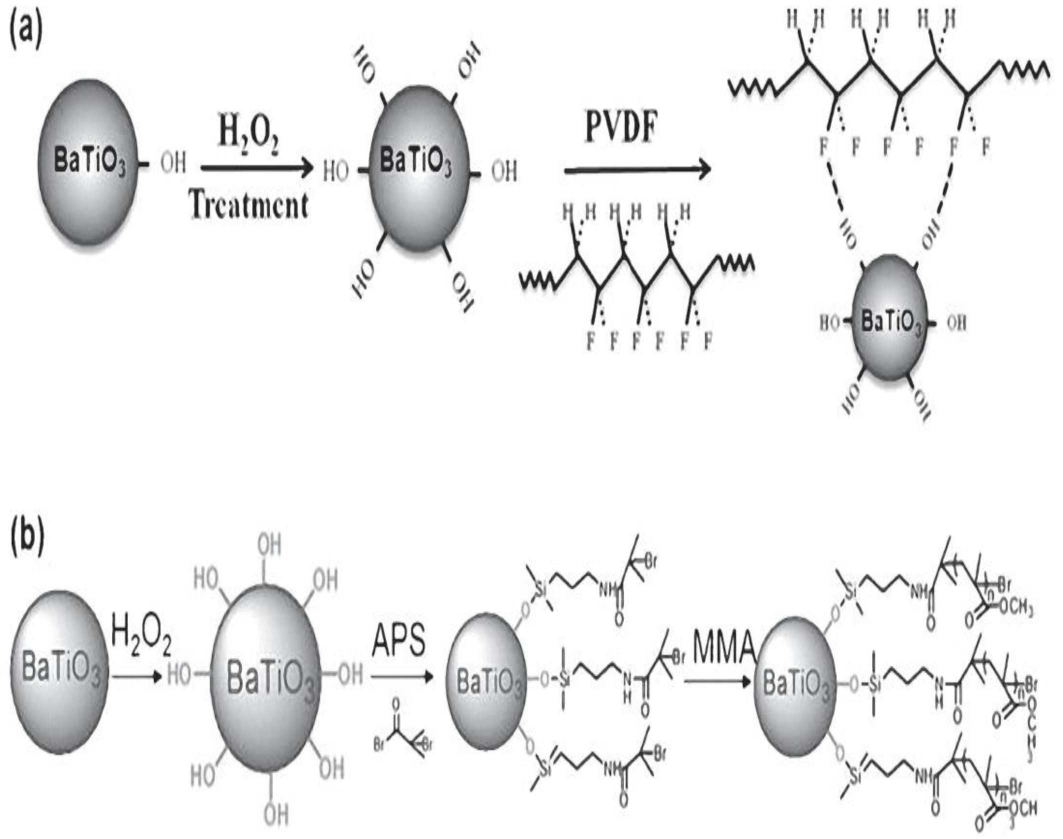

Fig. 1.21 (a) Schematic representation depicting the hydroxylation of $BaTiO_3$ nanoparticles and the establishment of hydrogen bonds in hy-$BaTiO_3$/PVDF composites, (b) Illustration outlining the in situ atom transfer radical polymerization process of MMA monomer initiated from the surface of $BaTiO_3$ nanoparticles[122].

The $BaTiO_3$ core enhances the permittivity (~ 16), while the flexible PMMA shell provides good dispersibility and inherent low dielectric loss for the base polymer as shown in Fig. 1.22.

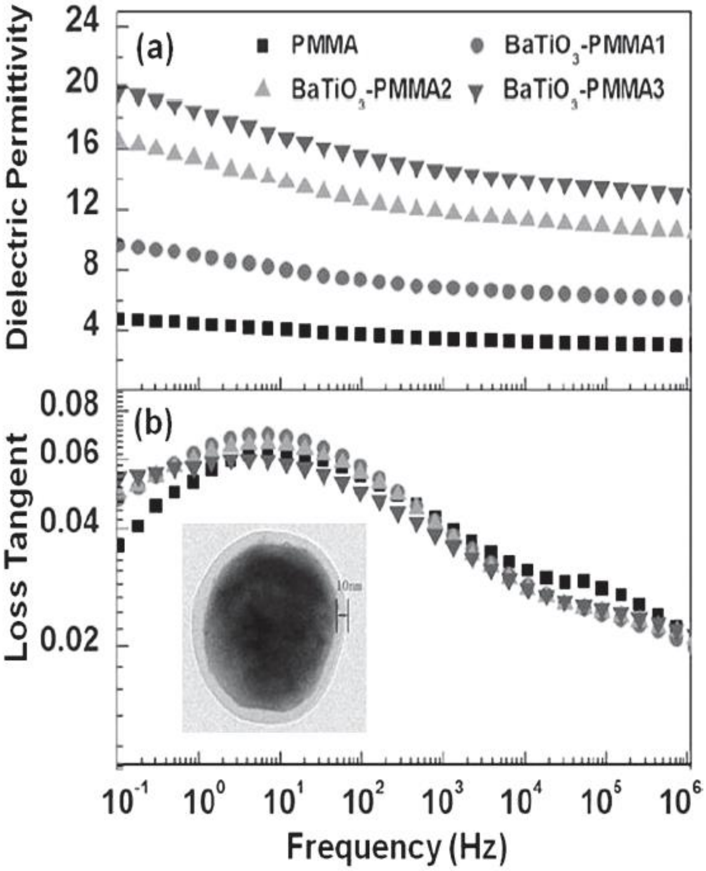

Fig. 1.22 Variation of (a) dielectric permittivity and (b) loss tangent with frequency for $BaTiO_3$/PMMA nanocomposites[122].

Samal et al have synthesized $BiFeO_3$/PVDF composites using PVDF polymer as a matrix and hydroxylated $BiFeO_3$ with H_2O_2 as a filler [123]. Hydroxylated $BiFeO_3$ has increased compatibility of bonding with ferrite. The surface hydroxylation has improved the interfacial interaction between filler and polymer matrix due to presence of strong hydrogen bonding in presence of -OH group. Thus improved dielectric and energy storage properties has been obtained which can be seen from Fig. 1.23.

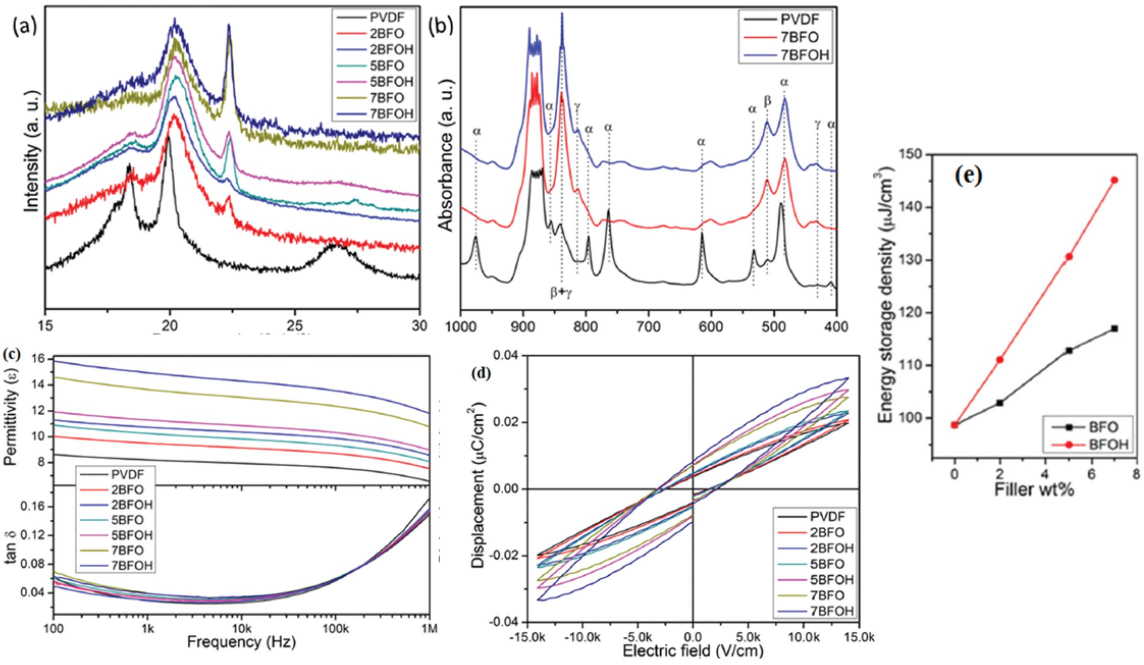

Fig. 1.23 (a) XRD analysis, (b) FTIR spectra, (c) variation of dielectric constant and dielectric loss with frequency, (d) D-E hysteresis curve, (e) variation of energy storage density with filler content[123].

1.13 Application of PVDF based nanocomposite film

Polyvinylidene Fluoride (PVDF) is a famous polymer material known for its excellent mechanical and electrical properties. When combined with other materials to form nanocomposites, the resultant films can exhibit enhanced characteristics suitable for various applications. Various applications of PVDF-based nanocomposite films are as follows:

- **Energy Harvesting**: The piezoelectric properties of PVDF make it an excellent material for converting mechanical energy into electrical energy. PVDF-based nanocomposite films can be used in energy harvesting devices like shoes or backpacks to generate electricity from everyday movements.
- **Sensors and Actuators:** The sensitivity of PVDF to mechanical stress makes it an excellent material for sensors. PVDF-based nanocomposite films can be used in

various types of sensors, such as pressure sensors, force sensors, and acoustic sensors. PVDF-based nanocomposite films can be used in sensors for environmental monitoring. For example, they can be used to detect changes in air pressure, humidity, or the presence of certain gases. PVDF-based nanocomposite films can also be used as actuators, converting electrical energy into mechanical motion. This can be used in various applications, including medical devices, robotics, and microelectromechanical systems (MEMS).

- **Wearable medical devices:** Due to their flexibility and biocompatibility, PVDF-based nanocomposite films can be used in wearable electronics. This could include smart textiles, health monitoring devices, and flexible displays. The biocompatibility of PVDF makes it suitable for bioengineering and biomedical applications. PVDF-based nanocomposite films can be used in tissue engineering, drug delivery systems, and artificial organs.
- **Supercapacitors and Ferroelectric Memory Devices:** By incorporating nonconducting/semiconducting/conducting materials into PVDF, the resultant nanocomposite films can be used in supercapacitors. This can enhance energy storage capabilities for various electronic devices. The ferroelectric properties of PVDF can also be utilized in memory devices. PVDF-based nanocomposite films can be used as ferroelectric memory elements in non-volatile memory devices.

In conclusion, the versatility and unique properties of PVDF-based nanocomposite films make them suitable for a wide range of applications across various industries. These applications support the enhanced mechanical, electrical, and piezoelectric properties of the nanocomposite films.

1.14 Motivation of the thesis

The main encouragement towards my present research work was to study the role of PVDF in PVDF based polymer ceramic composites using PVDF as a filler and ceramic as matrix. The main motive of my present research work is to develop PVDF based composite material for capacitive energy storage application. In present research work, I have synthesized three different PVDF based composites with PVDF as a filler in one composite and matrix in other two composites. PVDF based polymer composite with polymer as a filler was synthesized in compact pellet form using cold sintering method and composite with polymer as a matrix was synthesized in thick film form using solution casting method. The composite films were synthesized using H_2O_2 surface modified ceramic nanofiller for better dispersion in the PVDF polymer matrix. The dielectric and energy storage properties of the synthesized PVDF based polymer composites were studied.

1.15 Objectives of the present research work

As we have seen from different reported literature, ceramics have high dielectric constant but low dielectric breakdown strength and polymers have high dielectric breakdown strength but low dielectric constant. In this regard, Polymer based composites have been synthesized with various filler and matrix to enhance the energy storage properties. In polymer matrix mainly two type of materials namely conducting and ceramics has been reinforced to enhance the energy storage properties.

The important objectives of the present research work are as follows:

1. The selection of suitable polymer material for the synthesis of polymer-based composites. Here, we have chosen PVDF as a polymer material to synthesize polymer-based composites due to its highest dielectric constant among all known polymers.

2. The selection of suitable ceramic material is another aim for polymer-based composites. Here, we have chosen $Ba_{0.7}Sr_{0.3}TiO_3$, $BaZrO_3$ and $Ba_{0.4}Zr_{0.6}TiO_3$ as a ceramic material due to its high dielectric constant.
3. To study the dielectric and energy storage properties of as synthesized PVDF based composites for capacitive energy storage application.
4. To study the effect of surface hydroxylation of nanofillers in the polymer matrix.
5. To study the dielectric breakdown strength of the as synthesized PVDF based composite materials.

In this regard, following PVDF based polymer composites have been synthesized and their dielectric and energy storage properties have been studied.

1. Energy storage properties of cold sintered $Ba_{0.7}Sr_{0.3}TiO_3$/PVDF Polymer Ceramic Nanocomposites.
2. $BaZrO_3$/Poly (Vinylidene difluoride) Ceramic Nanocomposite Films with Improved Dielectric and Energy Storage Properties.
3. $BaZr_{0.4}Ti_{0.6}O_3$/Poly (Vinylidene fluoride) Composite Films with Improved Dielectric and Energy Storage Properties.