Chapter 6
Effect of Nanofillers-Reinforced Polymer Blends for Dielectric Applications

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Abstract The dielectric properties of nanofiller-reinforced polymer blends were discussed in this chapter. The fast development of modern technology means that innovative, eco-friendly, flexible, cost-effective, and light materials must be made for human development. This chapter study looks at the wide range of dielectric materials discovered, from ceramics to polymer composites, and the principles that led to their use in real-world applications. This chapter has outlined the fundamental concepts of dielectric behavior in composite systems. This chapter also looks at how polarization models produce composites to give them suitable dielectric properties and combinations of the different composite parts to solve engineering and scientific problems. Also, recent discoveries of dielectric composite materials have been put into groups, and their properties have been examined. This chapter discusses polymer-ceramic dielectric composites, ceramic-based dielectric composites, natural fiber-reinforced polymer composites (NFRPCs), and bio-based polymer dielectric composites. Finally, the production procedures of all of the dielectric materials discussed, as well as their key applications, have been carefully investigated.

Keywords Polymer dielectrics · Dielectric materials · Ceramic dielectrics · Characterization of materials

6.1 Introduction

The introduction of electricity to the globe ushered in a period of rapid and profound change that was impossible to foresee. The intelligent people on this planet have been eager to use the sciences and theories that electricity has made possible to look into the unknown and spread information about it. Soon after that, in the 1700s and 1800s, much progress was made that led to the basic ideas that make induction an excellent way to produce electricity. Since then, scientists and engineers have kept

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looking into ways to make electricity. This has led to the invention of light bulbs, which have brought light to parts of the world that were previously in the dark [1].

Regarding any aspect of innovation, the material employed is a primary consideration [2]. This is because different materials have different properties that change the need for the invention. Because of this, materials science and engineering research have become an essential part of many of the world's most important discoveries. Over the past 50 years, improvements in technology related to semiconductors, lasers, microscopes, light-emitting diodes, lithium-ion batteries, nanoparticles, fiber-reinforced plastics, and metamaterials have been made possible, thanks to advancements in materials and research in material science [3]. Only because of the progress made in materials science, these researchers have been able to find breakthroughs in their respective domains. Material science is essential in almost every part of modern life, from making a pen's capillary tube to a high-resolution lens for a space mission. In addition to this, they have shown the critical role that materials engineering plays by breaking barriers in the fields of aeronautics, medicine, and information technology.

Dielectrics research is one of the most intriguing fields in materials science and electronics. Michael Faraday, a famous scientist, was the first to use this term to describe the occurrence that occurred when an insulating material was placed in between an electric field and the object being tested. When the insulator underwent charge distribution and storage for a limited duration, this factor was eventually shown to represent a sort of polarization. Capacitors, which utilized insulating materials or a dielectric substance to store charge and, in turn, energy, were invented thanks to Faraday's principles. Since that time, the fields of electronics and materials have advanced to create new dielectric materials that may be employed in applications such as capacitors, pulsed power release, integrated circuits, battery storage, and piezoelectric materials [4]. It is unquestionably anticipated that the nature of materials and their behavior would improve with the fast growth of global markets and technological breakthroughs.

This chapter covers the fundamental theory, fundamental quantities, and fundamental principles of the dielectric. This chapter discussed the basic variables that affect the dielectric as well as the method used to test the dielectric. Additionally, we discussed the high-K and low-K dielectric qualities using several polymer categorization schemes based on permittivity. Dielectric materials based on polymers and their composites are made from a variety of materials, including those with ceramic, carbon, and semiconducting bases. We explained the dielectric qualities and their imitators in the electrochemical application in several instances.

6.2 Dielectric Fundamental Theory

William Whewell created the term dielectric, which derives from the Greek word 'Di' or 'Día' means across and electric. "Dielectric" and "Insulator" are synonyms. Dielectric materials have few free or loosely bound electrons and a high specific resistance, which slows down the flow of electricity. Charge carriers do not move

through a dielectric material when an electric field is present. Instead, their equilibrium positions just move a little bit. A positive charge moving along the direction of an applied electric field creates an electric dipole moment. Polarization is the number of dipole moments per unit volume. Due to opposing charge separation, an internal electrical field opposes the material's external field. Random orientation deployments result in zero internal fields without external fields. Direct or alternating current will transfer electric charges via any conductor or insulator. If the material is an insulator or dielectric, the movement of these charges will be hindered, forming a dipole moment between the two substances and polarizing them. To improve material qualities and comprehend dielectric behavior, we must grasp numerous fundamental quantities.

6.2.1   Electric Dipole Moment

An electric dipole is made up of two point charges that are equal and opposing one another, and they are separated by some distance. A dipole moment will be the term used to describe the ensuing occurrence, and polarization will be the term used to describe the accumulation of dipole moments inside a volume. When all of the dipole charges are aligned in the same direction, the polarizability of the material will be determined by the number of dipole moments that are contained inside each unit. Since the dipole moment contains a component that specifies the direction of the dipole moment that it generates, it is a vector quantity.

When two charges, $+q$ and $-q$, are separated by a distance r, the electric dipole moment, denoted by m, is a vector with magnitude $m = qr$ and a direction from the negative charge to the positive charge. When placed in an electric field from the outside, an electric dipole experiences a torque equal to the product of m, E, and the sine of the angle between m and E ($\tau = mE \sin\theta$). Torque has a tendency to align the dipole moment, denoted by m, in the direction of E. The orientation of dipole moments in the presence of an external electric field is shown in Fig. 6.1. If materials have n numbers of an electric dipole, then the total dipole moment is represented by the given equation,

$$M = \sum_{i=1}^{n} q_i r_i \tag{6.1}$$

where i represent the ith number of dipole moments. The polarization (P) of a dielectric material is defined as the dipole moments per unit volume.

$$P = \frac{M}{V} \tag{6.2}$$

where V volume of the dielectric materials.
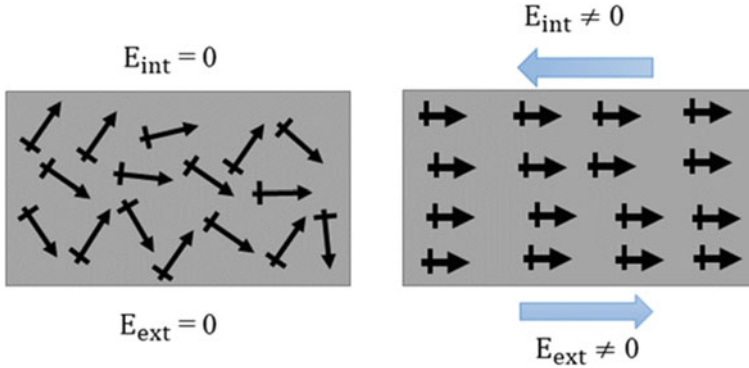
Fig. 6.1 Orientation of dipole moments in the presence of the external electric field

The formula for calculating the potential energy of a dipole is $U_e = -pE \cos$, which may also be written as $U_e = -p \cdot E$ in vector notation. In an electric field that is not homogeneous throughout, the potential energy of an electric dipole will vary depending on its location, and the dipole will be able to experience a force. When p is aligned with E, the direction of decreasing field strength corresponds to the order in which the force acting on the dipole will be. This is because the potential energy U_e will decrease in this direction.

6.2.2 Dielectric Constant

The charge density (*D*), or dielectric displacement caused by an applied electric field *E* in a dielectric medium is proportional to the magnitude of the field. This direct proportionality necessitates the inclusion of a constant, denoted by the symbol $k(\varepsilon)$, which represents the dielectric constant or permittivity of the material that is sandwiched in between the parallel plates.

$$D = \varepsilon E \tag{6.3}$$

An absolute permittivity (ε_0) is discovered to exist in a vacuum, which is the location where the electric field is produced, and this property will be expressed as follows:

$$D = \varepsilon_0 E \tag{6.4}$$

The absolute permittivity is 8.854×10^{-12} F/m because there is no air to interact with. Accordingly, the dielectric constant (also known as the relative permittivity) may be thought of as the density of the electric field created in the medium divided by the density of the electric field generated in a vacuum when the electric field

is held at a constant. It is also the ratio between the material's capacitance and the vacuum's capacitance. This section describes the potential difference between the parallel plates under certain situations:

$$V = |E_0|r \tag{6.5}$$

The decrease in field strength and the potential difference that results from the addition of a dielectric material between two parallel plate conductors is indicative of the charge storage capacity of the dielectric material. For all practical purposes, the static dielectric constant may be expressed in terms of capacitances in a vacuum and with a dielectric in the center. Here is the permittivity or dielectric constant equation.

$$E_0 = \frac{C}{C_0} \tag{6.6}$$

In addition, the capacitance of the circuit, while it is empty or under vacuum, is denoted by the letter C, whereas the capacitance when it is filled with the dielectric material is denoted by the letter C_0. Although this word is not often used, permittivity has a link to electrical susceptibility. According to one idea, the permittivity values of materials are determined by their electrical susceptibility.

6.2.3 Dialectics Under the Applied Electric Field

A dielectric material's properties may be studied by applying an electric field. Polarization, dissipation, conduction, and breakdown are important characteristics of materials. Direct current aligns dipoles in a dielectric material's field direction. Furthermore, the charge migrates from one end to the other, ensuring polarization. By neutralizing electrode charges, dielectric substances store charge and act as capacitors. The permittivity of a substance is determined by its capacitance value. There are two types of current in an alternating current electric field between parallel plate capacitors. A charging current (I_C) and a loss current (I_L) determine the material's dielectric constant. The loss current is the parallel material's conductance. Some polarization and conduction currents are the same.

$$I = I_C + I_L \tag{6.7}$$

Dielectric constants may be used to indicate charge storage, where the aforementioned equation may be changed.

$$I = V(i\omega C_0)(\epsilon' - i \epsilon'') \tag{6.8}$$

$$\varepsilon^* = \epsilon' - i \epsilon'' \tag{6.9}$$

One rotation of the object is equal to $\omega = 2\pi f$ (radians per second), where the AC voltage supply's frequency is f (Eq. 6.8). $\in'$ is the real part of the dielectric constant, and $\in''$ is the imaginary part of the dielectric constant, where ε^* represents the electrical losses in the dielectric material. The dielectric constant may be stated to better explain electric losses, a complicated number in relation to Eq. (6.9). When charging is in progress, the charge is stored in the material because of polarization, and when an alternating current is flowing, the phase of the polarization current is 90 degrees out of phase with the external electric field, contributing to losses or dielectric dissipation. Loss current is a current that runs through resistance and causes energy loss. It is regarded as one of the most significant dielectric losses in the critical elements that engineers, among others, find interesting to determine the suitability of a material for the task at hand. When a capacitor is placed between parallel plate electrodes in a vacuum, the voltage is shown as follows:

$$v = V_m \cos \omega t \tag{6.10}$$

The current through the capacitor is introduced as i_i, where v represents the instantaneous voltage, V_m represents the maximum value of v, and ω represents the angular frequency.

$$i_i = I_m\left(\cos \omega t + \frac{\pi}{2}\right) \tag{6.11}$$

And I_m can be represented by,

$$I_m = \frac{V_m}{z} = \omega C_0 V_m \tag{6.12}$$

The optimum dielectric material has a current–voltage relationship of 90, when the voltage and the current components are not in phase. When a result of the increase in capacitance caused by the dielectric material being positioned between the electrodes, the current is as follows:

$$i_i = I_m Cos\left[\omega t + \left(\frac{\pi}{2} - \delta\right)\right] \tag{6.13}$$

$$I_m = \omega C_0 V_m \in \tag{6.14}$$

In the equations shown above, the dimensionless dielectric constant is introduced. When the current and voltage are out of phase at an angle of 2°, this angle is known as the loss angle in Eq. (6.11). The current between the electrodes may be split into two halves. While the charging current is identical to that of an ideal capacitor, the dielectric loss is located in the 90° trailing component of the applied voltage, and the corresponding equation for the loss angle is,

$$\delta = \tan^{-1} \frac{\varepsilon''}{\varepsilon'} \tag{6.15}$$

As a result, tan is known as the dissipation factor, and ε'' is known as the loss index. As a result, the loss index in a dielectric material is defined as the complex portion of the dielectric constant, and the dielectric loss may be calculated using the equation above. The letter D is used to symbolize the dissipation component, tan, commonly known as the loss tangent. The following Eq. (6.18) may also be expressed in terms of the charging current and loss current.

$$\tan \delta = \frac{I_L}{I_C} = \frac{\varepsilon''}{\varepsilon'} \tag{6.16}$$

The loss factor may be expressed in another equation when it comes to resistance and impedance in a capacitor, supposing the resistance is a theoretically infinite quantity.

$$\tan \delta = \frac{1}{\omega RC} \tag{6.17}$$

6.2.3.1 Polarization

Polarization is the spatial organization of a charged particle in response to an applied electric field. In order to counteract the effects of the electric field, the charges will become polarized. This will result in the negative charges moving in opposite directions. The presence of an external field is what leads to the generation of an electric moment over the whole of the dielectric material's volume, and this occurs in each polarizing unit, whether it is an atom, an ion, or a molecule. The polarizable unit will acquire an electric dipole moment, denoted by the symbol p, whose magnitude is proportional to the strength of the external field, denoted by the symbol E. This direct proportionality is shown by linear dielectrics and is given by the equation $p = \alpha E$, where $\alpha = $ polarizability, which represents the qualities of individual polarizable units and is denoted by a symbol. Linear dielectrics exhibit this direct proportionality.

The degree to which a dielectric substance may be polarized is crucial in determining its electrical characteristics. This parameter is independent of the dielectric volume; therefore, it is very crucial. Because polarization causes charges that may be displaced to collect at physical barriers like grain boundaries, interfacial polarization, and space-charge polarization can both be said to have occurred as a consequence of polarization. Dielectric behavior may be caused by several different dielectric processes, which can be seen at the microscopic level. The dielectric constant is determined by the polarization process, which changes with frequency. At microwave frequencies, for instance, the dipole of water molecules, which spins in response to an alternating electric field, interacts strongly with ionic conduction. This happens

because water molecules are polarized in a way that allows them to conduct electricity. Atomic and electrical mechanisms are, on the whole, quite feeble. Each dielectric mechanism has a unique "cutoff frequency" as a defining property.

Dipole moments per unit volume are called the polarization of dielectric materials. If the materials have n numbers of dipole moments, then the total polarization of the materials is defined as,

$$P = \sum_{j=1}^{n} m_j \tag{6.18}$$

In the case of polar materials, there are permanent dipole moments. Due to the random arrangement's dipole moments, the resultant dipole moments of the materials are zero, but if the materials applied a strong electric field, then the materials showed two types of phenomenon, one is intrinsic dipole moments (m_i) which tends to align along the direction of the electric field to provide a net dipole moment, and the second is induced dipole moments (m_{ind}) developed in the material.

$$m_T = m_i + m_{ind} \tag{6.19}$$

Based on the polarization mechanism, dielectric polarization is divided into five major categories such as.

1. Electronic polarization (P_e),
2. Ionic or atomic polarization (P_a),
3. Orientational polarization (P_{or}),
4. Space-charge/interfacial polarization (P_{sp}),
5. Spontaneous polarization (P_{st}).

$$P = P_e + P_a + P_{or} + P_{sp} + P_{st} \tag{6.20}$$

It takes a certain amount of time for the dipoles' dielectric polarization to reach its maximum value when an external field is applied. The dipoles' dielectric polarization will diminish after some time when the external field is no longer there. The polarizations of the dipoles in the material and the alterations to the electric field occur at different times. An example of relaxation is when polarization (dipole alignment) lags after an applied field. Because of the lag, Gibbs's free energy is always decreasing and can never be restored. Transmission, or relaxation, is a function of frequency. Debye relaxation refers to the phenomenon that occurs in ideal systems when the dipole populations do not interact and may be described by the Debye equation. When all the material's dipoles relax at the same rate (same relaxation time), that is, when the relaxation time is equal to 1, where is the angular frequency of the applied field, we say that the material is undergoing Debye relaxation. In most cases, it is written as the frequency dependence of the medium's complex permittivity.

$$\in (\omega) = \epsilon_\alpha + \frac{\Delta \in}{1 + i\omega\tau} \tag{6.21}$$

where ϵ_α is the dielectric constant at the highest frequency and $\Delta\varepsilon = \epsilon_s - \epsilon_\alpha$ where ϵ_s is the dielectric constant at the lowest frequency and τ is the relaxation time. Real and imaginary parts of the complex dielectric permittivity yield

$$\in (\omega) = \epsilon_\alpha + \frac{\epsilon_s - \epsilon_\alpha}{1 + i\omega\tau} \tag{6.22}$$

$$\epsilon' = \epsilon_\alpha + \frac{(\epsilon_s - \epsilon_\alpha)\omega\tau}{1 + \omega^2\tau^2} \tag{6.23}$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\alpha)\omega\tau}{1 + \omega^2\tau^2} \tag{6.24}$$

The dielectric loss is given by,

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} = \frac{(\epsilon_s - \epsilon_\alpha)\omega\tau}{\epsilon_\alpha + \omega^2\tau^2} \tag{6.25}$$

In contrast, many dielectric materials have multiple relaxation times for dipoles. This means that instead of the Debye equation, they adhere to the Cole–Cole equation.

6.2.3.2 Dielectric Relaxation

Response time to a periodic external electric field is a key issue in dielectrics. Dielectric relaxation occurs when polarization lags behind an oscillating electric field. Dielectric relaxation may occur at a typical period for a certain polarization; hence, it may assist to identify the polarization process. It also causes considerable energy loss (or conversion, like in an oscillator, etc.), which is vital for engineering applications. Because time t and frequency f are inverse ($f = 1/t$), dielectric relaxation is explored in the frequency domain through dielectric spectroscopy. Impedance analyzers (LCR meters) typically work from a few Hz to 10 MHz. A vector network analyzer works from MHz to GHz. Higher frequency spectroscopy uses wave-guided systems, THz time-domain spectroscopy, etc. In many circumstances, these techniques are not marketed.

Different electric parameters, such as the complex dielectric constant $\varepsilon^* = \varepsilon' - \varepsilon''$, the complex impedance $Z^* = Z' - iZ$, the complex admittance $Y^* = Y' - iY''$, and the complex electric modulus $M^* = M' - iM''$ may be used to elucidate a relaxation process. A material's electric modulus, which is equal to the inverse of its dielectric permittivity, represents the rate at which its electric field relaxes while the electric displacement remains the same ($M^* = 1/\varepsilon^*$).

Debye Relaxation

The Debye relaxation equation is the most straightforward and tasteful mathematical expression utilized to explain the phenomena of relaxation to date.

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \qquad (6.26)$$

The static and high-frequency dielectric permittivity are shown here as ε_s and ε_∞, respectively. The typical time for relaxing is τ. Peter Debye, a scientist, was the first to describe this relaxation for noninteracting dipoles in an alternating external electric field with a distinct relaxation duration. ε'-ε'' plots the optimal semicircle for Debye relaxation in the complex plane. The semicircle transforms into an ellipse, known as the Cole–Cole circle, as a result of the reciprocal interactions of dipoles in actual materials. The relaxation is known as Cole–Cole relaxation, and the following equation describes it:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \qquad (6.27)$$

Here, the value of the exponent parameter may range from 0 to 1. The Cole–Cole equation becomes the Debye equation when $= 0$. In various polymers, Cole–Cole relaxation is seen.

Maxwell–Wagner Relaxation

Electric inhomogeneities in materials, such as grain boundaries, the contact between dielectrics and electrodes, and others, generate Maxwell–Wagner relaxation. This is sometimes shown using a two-layer equivalent electric circuit, as in Fig. 6.2.

Maxwell–Wagner relaxation's dielectric permittivity may alternatively be stated as a Debye relaxation style:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} - i\frac{\sigma}{\omega} \qquad (6.28)$$

If the following conditions are fulfilled, the result will be: $C_0 = \varepsilon_0 S/d$; $\varepsilon_\infty = C_1 C_2/[C_0(C_1 + C_2)]$; $\varepsilon_0 = [R^2{}_1 C_1 + R^2_2 C_2]/[C_0(R_1 + R_2)^2]$; $\delta = 1/[C_0(R_1 + R_2)]$; $\tau = R_1 R_2(C_1 + C_2)/(R_1 + R_2)$. It seems to reason that when there is a large disparity between two resistances, the relaxation would be visible. Each RC unit in

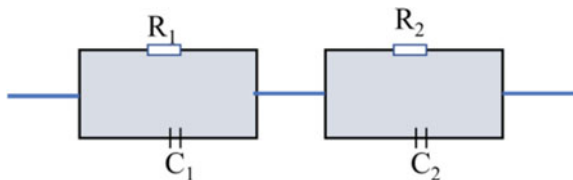Fig. 6.2 Two-layer Maxwell–Wagner equivalent electric circuit

Fig. 6.2 corresponds to a component of the researched dielectrics, such as a grain, grain border, or electrode interface. It is usual practice to plot data in both impedance and electric modulus to distinguish between these various component relaxations. The circuit's impedance is as follows:

$$Z' = \frac{R_1}{1 + (\omega R_1 C_1)^2} + \frac{R_2}{1 + (\omega R_2 C_2)^2} \tag{6.29}$$

$$Z'' = R_1 \frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2} + R_2 \frac{\omega R_2 C_2}{1 + (\omega R_2 C_2)^2} \tag{6.30}$$

The electric modulus of the circuit is as follows:

$$M' = \frac{C_0}{C_1} \frac{(\omega R_1 C_1)^2}{1 + (\omega R_1 C_1)^2} + \frac{C_0}{C_2} \frac{(\omega R_2 C_2)^2}{1 + (\omega R_2 C_2)^2} \tag{6.31}$$

$$M'' = \frac{C_0}{C_1} \frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2} + \frac{C_0}{C_2} \frac{\omega R_2 C_2}{1 + (\omega R_2 C_2)^2} \tag{6.32}$$

From these equations, we may deduce that, whereas normalizing the electric modulus shows just a little amount of relaxation in capacitance, normalizing the impedance reveals a significant amount of relaxation in resistance. In light of the fact that the electric circuit corresponding to Maxwell–Wagner relaxation changes from case to case, a more complex circuit model may be utilized to characterize the dielectric behavior of Maxwell–Wagner relaxation. Here, we just provide the simplest scenario, which calls for the use of only two dielectric constituents.

Universal Dielectric Relaxation

The term universal dielectric response also refers to universal dielectric relaxation. We first present complicated conductivity to help you grasp it better.

$$\sigma = \sigma_0 + \sigma' - i\sigma'' \tag{6.33}$$

In this case, the DC conductivity is σ_0, and the AC conductivity is σ'. It is unclear if the formula has a value of σ_0. You may look at the link between σ_0 and σ as $\sigma_0 = \lim \sigma$ as $f \to 0$. Typically, the AC conductivity is determined from dielectric measurement by:

$$\sigma = \varepsilon_0 \varepsilon'' \omega \tag{6.34}$$

Jonscher observed that the frequency-dependent AC conductivity for several dielectrics complies with the following exponent connection.

$$\sigma = A\omega^n (0 < n < 1) \tag{6.35}$$

This is referred to as "universal dielectric relaxation". It is referred to as a "virtually constant loss" if $n = 1$. The ion hopping effect is thought to explain the universal dielectric response. But at high frequencies, electric heterogeneity may also cause similar phenomena. At sufficiently low temperatures or high frequencies, almost continuous loss occurs, and the cause was formerly thought to be vibration relaxation or off-center relaxations that spread out into a wide distribution.

It has so far been unable to pinpoint a particular relaxation. The temperature typically has a considerable impact on the characteristic relaxation time constant, which may be described as an exponent function of temperature:

$$\tau = \tau_0 e^{E_a/k_B T} \tag{6.36}$$

Here, the temperature is T, the Boltzmann constant is k_B, and E_a is the activation energy. The activation energy is a reflection of the power required for dipoles to jump from one potential well to another. As a result, it provides details on potential relaxation mechanisms.

6.3   Techniques for Dielectric Measurements

When it comes to measuring dielectric properties, there is no one method that can describe all materials throughout the whole frequency range. Because it is difficult to get an accurate measurement for both kinds of materials (lossy and low loss), it means that each band and their respective losses need a distinct procedure. When attempting to characterize materials based on their dielectric measurements, there is always some degree of ambiguity. Some significant factors on that the whole process depends,

- Temperature,
- Nature of the materials,
- Thickness of the materials,
- Size of the materials,
- Frequency,
- Coating and non-coating,
- Destructive and nondestructive,
- Sample cost,
- Sample prepetition process.

Considering the above parameters, testing frequency and test material should be addressed while choosing a measurement procedure. Even the measuring equipment, sample holder, and design are determined by frequency and substance. As for measurement techniques, they may be divided into two primary categories: resonant and non-resonant. Materials may be characterized at single or several discrete frequencies using resonant techniques. This method employs a dielectric material as the resonant element. However, it is applicable only to test samples with minimal loss.

Resonators that are dielectric, planar, and split are all good examples. Perturbation and perturbation-induced resonant frequency shift are two further techniques. This approach suits low- to moderate-loss samples. Non-resonant methods may measure a wide frequency range. It may classify materials by calculating their reflection and transmission coefficients. Here are several prominent and relevant dielectric measuring methods.

6.3.1 Coaxial Probe Method

A coaxial probe, coaxial-line probe, or open-ended coaxial-line technique are all terms used to describe this kind of probe and its associated technology. Measuring lossy materials at high frequencies (such as RF and microwave) may be accomplished using this approach, which is one of the most practical and regularly used methods. In order to measure the complex reflection coefficient, it is used with the VNA.

A metallic probe is used by the coaxial line in order to detect the reflected signal (both phase and magnitude) from the MUT. When testing liquids, the probe is submerged into the sample, but when testing flat surfaces, it contacts the sample. Dielectric measurements may be carried out using this approach across a wide frequency range, anywhere from 0.5 to 110 GHz, and the process itself is relatively straightforward. However, this technique exhibits some deflection for the measurements of low-permittivity materials across a large frequency range of around 0.5–110 GHz [5]. However, some deflection may be seen using this approach for materials with a low permittivity (Fig. 6.3).

6.3.2 Transmission Line Method (Waveguide)

Another common method involves placing a sample of the chemical under examination in the center of a closed transmission line (as shown in Fig. 6.4). When taking measurements, both the reflection and transmission coefficients come in handy. Although it outperforms the coaxial line in terms of precision and sensitivity, the frequency range that it is capable of is much less than that of the coaxial cable. Because a sample has to span the whole cross-sectional area of a line, it needs to be prepared in the shape of a slab or an annular geometry slab. This makes sample preparation very complicated and, as a result, more time consuming.

6.3.3 Free-Space Method

This approach is risk-free since it does not require physical touch. Though often used at a higher frequency, it is also capable of being employed at a lower one; however,
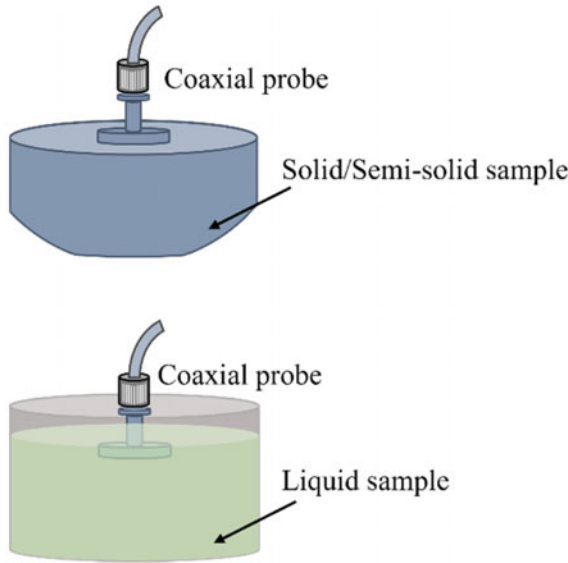
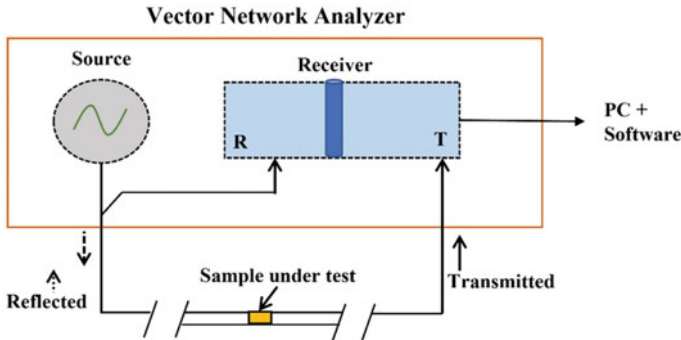**Fig. 6.3** Schematic diagram for coaxial probe method [6]

Fig. 6.4 Schematic diagram for transmission (waveguide) line method [7]

the latter application is restricted in terms of the sample sizes it can practically handle. The dielectric properties of solid materials are measured using the free-space approach, which requires the samples to be big, flat, and properly faced on both sides. Homogeneous materials are those that are uniform and free of any imperfections. Material is positioned in between two horn antennas to direct energy onto or through the material in combination with a vector network analyzer. The use of the free-space measurement approach has several benefits, the most important of which is the ability to get reflection and transmission coefficients without making any kind of physical contact with the sample (Fig. 6.5).
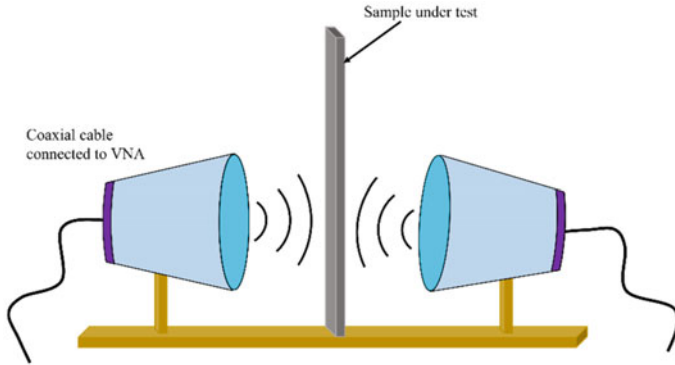
Fig. 6.5 Schematic diagram for free-space method [8]

6.3.4 Resonant Cavity Method

This method does not involve any physical contact and is not harmful. It is most often used at a higher frequency, but it can also be used at a lower frequency; however, the latter application is restricted in terms of the sample sizes it can practically handle. The dielectric properties of solid materials are measured using the free-space approach, which requires the samples to be big, flat, and properly faced on both sides. Homogeneous materials are those that are uniform and free of any imperfections. Material is positioned in between two horn antennas with the intention of directing energy onto or through the material in combination with a vector network analyzer. The use of the free-space measurement approach has a number of benefits, the most important of which is the ability to get reflection and transmission coefficients without making any kind of physical contact with the sample (Fig. 6.6).
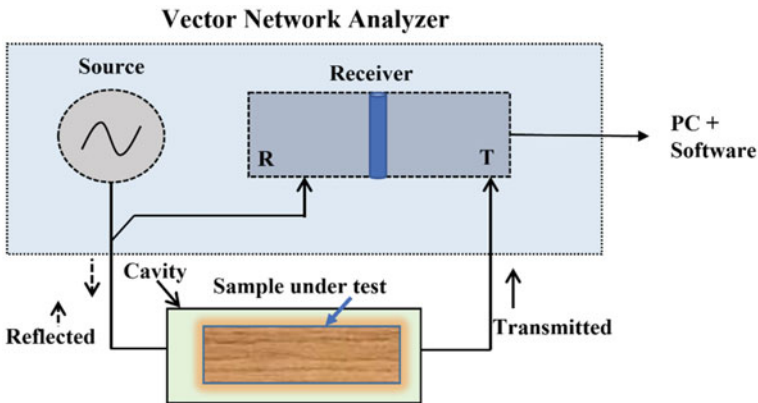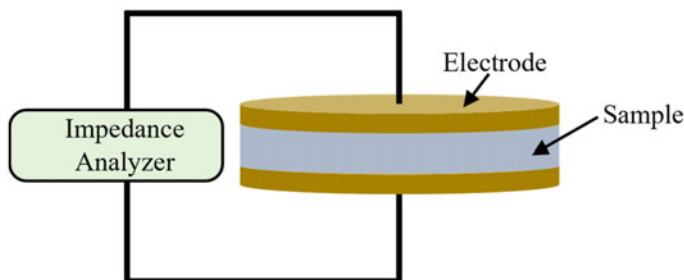

Fig. 6.6 Schematic diagram for cavity resonator method [7]

Fig. 6.7 Schematic diagram for parallel plate method [6]

6.3.5 Parallel Plate (Electrode) Method

To create a capacitor using the parallel plate capacitor technique, a dielectric material is placed between two electrodes in the form of a thin sheet sample in order to create a capacitor. The LCR meter, an impedance analyzer, and a dielectric fixture are the three instruments that may be used to collect measurements (see Fig. 6.7). In this technique, generally low frequencies of less than one gigahertz are used. When doing a test using parallel plates, it is necessary to take into account the size of the material as well as measure its capacitance and dissipation factor. In order to determine the dielectric constant of a material, a dielectric sample must first be placed in a sample holder before the capacitance value can be used to determine the permittivity. It includes extremely easy sample preparation and setup, and the frequency range that is generally used for this purpose is from 20 Hz to 1 GHz. It has a high measurement precision (approximately 1% for r' and 5% 0.005 for tan), and it has several other benefits as well. If the air gap and its consequences are not taken into consideration and calibrated, however, this may lead to substantial inaccuracy. Poor results are also brought about by the influence of electrode polarization, which leads to false observations. It is possible to lessen its impact by using electrodes with a large microscopic surface area or by operating at higher frequencies; this is because the effect weakens significantly with rising frequency [3].

6.3.6 Planar Transmission Method

These different kinds of transmission lines find widespread use in a variety of RF and microwave components. The microstrip line approach is the most frequent and straightforward method for measuring dielectric materials. It is simple to construct, there are few costs associated with its production, and its small construction makes it particularly well-suited for use in industrial settings. For the purpose of determining the dielectric permittivity, the test sample may function either as a substrate (when the sample is solid) or as a superstrate (when the sample is either solid or liquid).

Fig. 6.8 Schematic diagram for planar transmission line method (View from the top side of MSL) [6]

Signal Strip   Sample under test
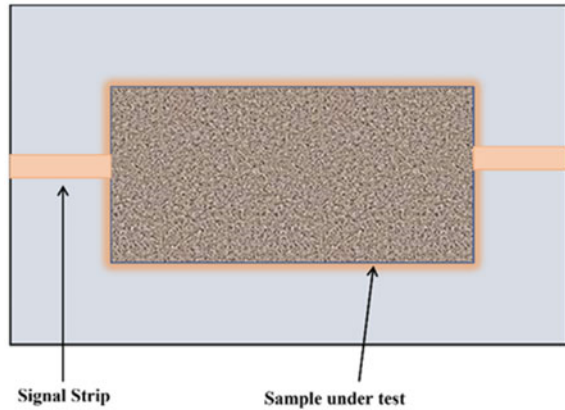
When a dielectric sample is placed over a quasi-TEM transmission line, it is generally known that the effective permittivity of MSL will change, a behavior that is highly dependent on the permittivity of the sample itself. In order to obtain the sample's dielectric characteristics, this will alter MSL's effective dielectric constant (εeff) and characteristic impedance (Z_0). First, you need to get the unloaded effective dielectric constant so you can take a reading. Then, you will need to attach the sample to the signal strip (as shown in Fig. 6.8). This study examines the alterations in the effective dielectric constant (εeff) and the characteristic impedance of a microstrip line (MSL). These changes can be utilized to determine the dielectric properties of a sample through the plane transmission line method. Bernard conducts dielectric measurements using a microstrip ring resonator. The approach demonstrates a change in the quality factor and a variation in the resonant frequency. When a sample is put on top of the ring, its presence alters the substrate or the air barrier, hence shifting the resonance frequency. When used as a substrate, rather than an overlay test material, the influence of the dielectric sample is able to shine through more clearly.

6.4   Dielectric Materials

Studies have revealed that polymers offer appealing qualities such as high flexibility, attractive chemical stability, cost efficiency, and simplicity of fabrication, which has led to their rising use in electronic applications [9]. Because polymers possess this inherent capacity, they may serve as viable substitutes for inorganic and ceramic-based dielectric materials. Polymers provide a number of benefits, but the fact that they have poor thermal stability and display poor dielectric constants restricts the majority of the applications to which they may be put. However, by manufacturing nanocomposites and including inorganic fillers in the composites, it is possible to enhance the dielectric constant values [10]. Research has been done on polymer dielectrics in many different aspects of their applications. One example is in the field

of microelectronics, which focuses primarily on the reduction in the size of electronic components [11].

6.4.1 Classification of Dielectric Materials

Dielectric materials are sometimes called "electrically insulating materials" materials because of their insulating qualities. Traditional dielectric capacitors may be categorized into several groups based on the various dielectric materials. First, there are dielectric materials based on polymers. This kind of capacitor mostly uses polymer materials as its dielectric materials. Then, there are dielectric capacitors made of ceramic. Such capacitors' dielectric components may be multi-phase ceramics, glass–ceramics, ceramic films, etc. Graphene and carbon nanotubes (CNT) are two examples of the types of carbon-based materials that are utilized to make dielectric materials. In a variety of contexts and applications, dielectric metal alloys made from oxides, sulfides, and nitrides of various metals are used. Perovskite materials are now being employed in applications that need them to be dielectric as well. In this chapter, we quickly go through every polymeric material and every composite that can be made from it.

6.4.2 Dielectric Polymer and Polymer–Polymer Composite Materials

Improving polymer breakdown strength is a challenge. Ramprasad investigated the process of polymer breakdown strength mathematically and found that dipoles increased dipole-induced scattering, which reduced and constrained hot electrons. Electron scattering by dipoles and phonons accounted for the temperature dependence of the breakdown field. Amorphous polymers have a high-voltage potential due to their randomly dispersed dipoles. Dipole scattering restricted mobility may analyze dipole scattering's effect on the polymer breakdown field. Because of their low cost, high dielectric strength, high energy density, and low dielectric loss, polymer-based dielectrics are preferable over ceramic dielectrics for various applications. Since these capacitors contribute a significant amount of space and weight (> 30%), further improvements in energy and power density of dielectric materials are necessary for miniaturization and better functionality in contemporary electronics and electrical power systems. High electric energy density with minimal dielectric loss is a key difficulty in producing polymer-based dielectrics. High-k polymer and low-k polymer and its composites play vital roles in the dielectric applications which are discussed below. All the polymer and polymeric composites were synthesized by different polymerization processes which are described in Table 6.1.

Table 6.1 List of the different polymerization process and their importance with examples

| Polymerization process	Methods and importance of the polymerization process	Example of polymer and its composites	Refs.
Sol-gel method	Because the synthesis process is done at room temperature and organic ingredients may be incorporated at the early phases of the reaction, the sol-gel approach is frequently employed in the preparation of polymer compounds. Polycondensation and hydrolysis may also occur concurrently to form glass-like polymer matrices. This process may also be used to create polycrystals and organic and inorganic substances	Sol-gel PPy	[12]
Melt blending	Melt blending, in which polymeric components are melted and chilled (cooled), is an efficient method for generating polymer composites	Clay/polymer composites	[13]
Solvent method	The solvent strategy employs a process called polymer intercalation from a solution, which is a solvent system in which the polymer or monomer may swell. Water, toluene, DMSO, DMF, and chloroform are the most common solvents used to dissolve the polymer into the intercalates	POP	[14]
Free-radical polymerization	A wide variety of polymers and material composites may be synthesized using the free-radical polymerization synthesis method. It is one of the most flexible types of polymerization because simple reactions may occur between polymeric free-radical chain ends and other chemicals or substrates due to the generality of free-radical chemical interactions	PMMA, PMMA-ZnS	[2, 15]
In situ polymerization	To initiate polymerization, a liquid monomer solution is absorbed by a modified silicate layer, where it then seeps into the void between the layers	PAni, PPy, PIn, etc	[16–18]
Spin-on technique	Making polymer thin films using spin-on or spin-coating requires dissolving soluble linear or branched polymers in a solvent. To evenly distribute the polymer solution, we place it in a jar and spin it at rates between 1,500 and 500 revolutions per minute	Macroporous polymer	[19]

(continued)

Table 6.1 (continued)

Polymerization process	Methods and importance of the polymerization process	Example of polymer and its composites	Refs.
Chemical vapor deposition	An electrically charged gas begins a reaction with plasma in polymer CVD, while the substrate temperature is adjusted independently. The coating material is heated, and the pressure surrounding the vessel is decreased, allowing the polymer plasma within the chamber to evaporate. The vapor is kept from settling on the substrate, resulting in a homogeneous covering. The thickness of the film deposition and the time required for the vaporization process are determined by temperature and pressure	Polysiloxane	[20]
Solvothermal	In solvothermal synthesis, the desired product is formed in solution using a closed-system technique that employs high temperatures and pressures to trigger a chemical reaction or breakdown of the precursor components	1D zinc coordination polymer	[21]
Electrochemical	Electropolymerization, or the production of polymer films in an electric field, typically uses either a constant potential (potentiostatic) or a linearly scanned potential (potentiodynamic) technique. Electropolymerization, or the production of polymer films using an electric field, typically makes use of either a constant potential (potentiostatic) or a linearly scanned potential (potentiodynamic) technique	PDMS	[22]
Hydrothermal	Hydrothermal synthesis is a common method used to create nanomaterials. It is simply a reaction-solution process. During hydrothermal synthesis, nanomaterials may be created at temperatures ranging from room temperature to thousands of degrees Celsius	Porous organic polymer	[23]

6.4.3 Low-k *Polymer and Its Composites*

If the dialectic permittivity of a polymer or polymer composite is less than 4.2, then the polymer or polymer composite may be referred to as having a low-*k* value. To reduce the permittivity of polymers, a number of different modifications can be applied to the polymer chains. Some examples of these adjustments include
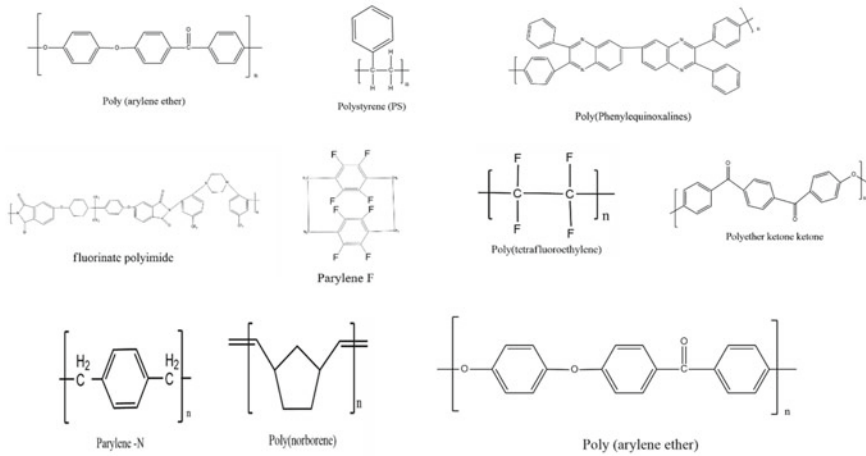
Fig. 6.9 Chemical structure of low-*k* polymer used for dielectric application

decreasing the ionic and orientation contributions and adding fluoride or carbon to the polymer chain.

Polymers, when used in dielectric applications, may be split into two categories: thermoplastic polymers and thermoset polymers. The addition polymerization process is most commonly used to manufacture thermoplastic polymers. Common thermoplastic polymers used in insulation systems include polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), and polyamide (PA). Insulation systems in electrical devices benefit greatly from the usage of thermoplastic polymers. In contrast, when heat or chemicals are used to cure thermostable or thermoset polymers, the polymerization process is irreversible and the resulting material cannot be altered. However, the composite's electrical and mechanical characteristics will undergo a cataclysmic shift due to treating these thermosetting polymers. These polymers are capable of taking on the shape of a resin. Epoxy, polyester, phenol, and silicon resins are all examples of these types of resins. The structure of low-*k* polymer is shown in Fig. 6.9.

6.4.4 Analysis of Important Low-k Dielectric Polymer

6.4.4.1 Dielectric Polymers Based on Silicon-Based Materials

These polymers are a hybrid mix with the formula RSiO3, where R may be any number of different things like alkyl, aryl, carboxylic acid, etc. Common silicon-based polymers with low dielectric permittivity and microwave losses include poly(hydrogen silsesquioxane) (PHSSQ) and polymethyl silsesquioxane (PMSSQ).

Table 6.2 At normal temperature, the dielectric permittivity of common traditional polymers

Polymer	Dielectric permittivity	Polymer	Dielectric permittivity
Poly(arylene ether)	2.9	Poly(arylene ether oxazole)	2.6–2.8
Polyquinoline	2.8	Poly(ether ketone ketone)	3.5
Poly(norbornene)	2.4	Silsequioxane	2.8–3.0
Polystyrene	2.6	Fluorinated polyimide	2.6–2.8
Poly(phenyl quinoxaline)	2.8	Poly(tetrafluoroethylene)	1.9
Polynaphthalene	2.2	Non-fluorinated aromatic polyimide	3.2–3.6
Parylene N	2.6	Parylene F	2.4

Because of their outstanding thermal, chemical, mechanical, and electrical capabilities, they have been widely researched for use in microelectronic packaging. The dielectric constants decreased gradually as frequency increased (2.96–2.55 from frequency ranges 100–1000 kHz). Dielectric loss rises with frequency, with a loss of 0.02–0.032 predicted from 100 kHz to 1 MHz [24].

The dielectric properties of nano-hybrid composites containing the silica-based polymer tetraethyl orthosilicate have been investigated. The dielectric properties of samples made by combining polyvinylpyrrolidone and silicon dioxide using the sol-gel technique in the presence of a coupling agent are studied. Dielectric constant and loss were determined using an impedance analyzer on samples with varying weight ratios. The estimated loss tangents demonstrate that when the silica concentration rises from 31.27 to 55.35 wt.%, the losses increase at low frequencies spanning from 1 to 100 kHz [25] (Table 6.2).

6.4.4.2 Low-*k* Epoxy Resins

Low-*k* dielectrics make use of epoxy resins. The properties they possess make them perfect for use in dental products. Their mechanical qualities, great adhesion strength, sensible heat, and electrical resistance make them ideal for application in coatings, adhesives, electronic materials, and polymer matrices for fiber-reinforced composites. Their primary use is as a microscale organic filler in dry distribution transformers. In order to create trifunctional epoxy resins, trimethylolpropane, and epichlorohydrin are combined. Low viscosity, noncrystalline, and plastic resin does not meet the application [26]. At low temperatures (127–348 °C), curing progresses slowly at first, then levels out after a few minutes. Epoxy systems that already include fluorine are modified with fluorinated monomers and oligomers for use in dielectrics. Fluorine boosts the blend's hydrophobicity but reduces its overall surface energy. Between 2 and 10 GHz, dielectric constants ranged from 6.8 to 5.5. Epoxy resins may be manufactured from biodegradable components such as sugars, starches, proteins, lipids, and oils. There is a high demand from business because of their low production cost,

small carbon footprint, and biodegradability. Epoxy resins may be made at a low cost by reacting soybean oil and castor oil with glacial acetic acid.

6.4.4.3 Fluorinated Polymers

Fluorocarbons are nonpolar, making them hydrophobic. Fluorinated polymers include at least one fluorine atom in the polymer chain, which limits water absorption. Fluorine may reduce the dielectric constant of polyimides. Fluorine hinders electronic polarization by being nonpolar and low-polarizable. Altering the polymer chain's free volume changes the composite's polarizability. PIs have strong chemical and thermal stability, and fluorine adds performance to electronics. Fluorination is used to enhance PI thin-film dielectric characteristics. Fluorine groups reduce surface free energy and dielectric permittivity of PI films, according to studies. When a reduction in dielectric constant is necessary, the fluorination procedure may be extended to epoxy resins. Epoxy resins have been used as insulation material because of their high electrical resistance and widespread use as molding compounds in electronic packaging. The regulated dielectric constants for fluorinated epoxy resins range from 2.71 to 3.25, and the related loss tangents have been estimated to be between 1.3×10^{-3} and 3.5×10^{-3}, respectively.

6.4.4.4 Porous Polymers

Hydrogen methyl silsesquioxane compounds, which provide low-k dielectric and loss properties, are promising porous polymers with low dielectric constants. They have a dielectric permittivity of 2.06 and have pores that are smaller than 10 nm in size because of their strong hydrogen bonding, which inhibits phase separation (on average). They are created by hybridizing the porous polymers with an amphiphilic block copolymer, namely poly[styrene-block-(2-vinylpyridine)] or PS-block-P2VP. The creation of regular nanopores in thin films is facilitated by this hybrid composite [27]. It is shown that the loss at 10 kHz is 0.04 and the dielectric constants are 3.6. The significant spontaneous polarization is what causes the consequences of these features. Additionally, the polymer chain's vast contact area leads to various interfacial polarizations [28]. The benefits of porous poly(vinylidene fluoride), often known as PVDF composites, in terms of mechanical strength, solvent resistance, and thermal stability make them valuable in applications involving multilayer dielectrics. At normal temperatures, PVDF composites have dielectric constants ranging from 7 to 13 [29]. Porous PVDF composites will have two compact surface layers and a dielectric permittivity of 1.5 to 2.5. Studies have shown the conductivity of copper nanowires in porous PVDF's dielectric behavior. When the number of nanowires was increased, low dielectric permittivity between 11.8 and 17.5 was observed. As the frequency was raised, the permittivity gradually decreased. Results from the dielectric permittivity have also shown that the Maxwell–Wagner–Sillars effect and interfacial polarization were identified.

6.4.5   *High-*k *Polymer and Its Composites*

In order to maximize performance, polymers with excellent dielectric properties at working frequencies and voltages are desired. These properties include high permittivity, low dielectric loss, and a high breakdown field [30]. High dielectric constant materials have a dielectric constant greater than silicon oxide ($k \sim 4.2$). The intrinsic dielectric constants of polymers have been increased using a variety of methods, including modifying the chain architecture of polymers, mixing polymers, dispersing ceramics, and conducting nanoparticles throughout polymers. There are many high-*k* polymers, which are good for dielectric application, and by the addition of other polymers to it, their dielectric properties increased. In this chapter, we described some important polymers and their composites for high-*k* dielectric properties.

6.4.5.1   Basic Polymer for High-*k* Dielectric Application

Polyvinyl Alcohol

Poly(vinyl alcohol), or PVA for short, is a water-soluble polymer having a high dielectric constant (between 5 and 8) between 10 Hz and 1 MHz, making it useful in low-temperature electronics. When PVA-infused composite substrates are cross-linked with an ammonium dichromate or another cross-linking agent, the resulting materials have a higher dielectric strength.

Polyvinylidene Fluoride

Mechanically flexible, low thermal conductivity, strong chemical and corrosion resistance, a dielectric constant of 8, and considerable dipole moments in the CH_2-CF_2 units all contribute to thermoplastic fluoropolymers' widespread usage as electrical insulators. With a leakage current of (4×10^{-6} A) or less, PVDF composite thin films are ideal for use in microelectronics. They are spin-coated on substrates whose amorphous phases at interfaces exhibit greater temperature relaxation. PVDF composites have a decent dielectric breakdown strength and minimal power dissipation compared to other high-*k* polymeric materials. PVDF composites with high dielectric constants may be employed in "gated" dielectric actuators, electric stress management, and capacitors [29]. There are various dielectric PVDF-based composites materials with dielectric loss and dielectic constant are tabulated in Table 6.3.

Cyanoethyl Polymers

CEP is an organic polymer with hydroxyl groups. A polysaccharide chain with a cyanoethyl side chain has a huge dipole moment. Their dielectric constant might

Table 6.3 Composites based on polyvinylidene fluoride (PVDF) and its dielectric property

PVDF-based composites	Filler materials	Dielectric loss	Dielectric constant	Refs.
PVDF-10 T	TiO_2	3.29	23.06	[31]
PVDF/PVA-MK (30%)	PVA and MK	0.1 (10^3 Hz)	4.27 (10^3 Hz)	[32]
PVDF/GO (20%)	GO	0.28	1.83	[33]
Zn/PVDF	Zn core–shell	3	60	[34]
$Ba_{0.6}Sr_{0.4}TiO_3$/PVDF	BST		8.7	[35]
$RuO_2@nBaTiO_3$/PVDF	$RuO_2@nBT$	1.467	3837.16	[10]

reach 16. Spin-coating CEP composites into thin films provides superior dielectric and semiconductor interfaces, like PVA composites. Cross-linking agents up to 50 wt% of CEP polymers reduce leakage current the greatest, meeting application requirements [36].

6.4.5.2   High-k Polymer–Polymer Blends and Composites

Polymer systems' desired qualities may be achieved through blending polymers with the right structure and properties in order to maximize the blend's permittivity. Researchers may create high-permittivity polymer blends by combining high-permittivity polymers with low-permittivity polymers. The improved permittivity comes from polymer–polymer interactions and novel mix topologies. The permittivity of polymer blend system (k_{blend}) is intermediate between components, $k_{polymer-A} < k_{blend} < k_{polymer-B}$. $k_{polymer-A}$ and $k_{polymer-B}$ are mix polymers. This blending process is a straightforward and effective path for organic materials, compared to other difficult synthetic procedures, generating excellent dielectric and mechanical characteristics, notably useful for capacitor manufacturing.

Researchers also have concentrated on polymer composites to boost the permittivity of polymer systems to fulfill electronic industry needs. High-permittivity polymer composites use various fillers distributed in the polymer matrix. Polymer composites will have high permittivity, great temperature stability, and frequency properties by mixing high-k inorganic materials with organic insulation. Two fillers are often used. High-k ceramic particles and electrically conductive additives like metals or carbon are used. These two additives improve polymer composites in various ways. Nanofiller agglomeration and poor compatibility between inorganic fillers and organic polymer matrices are major roadblocks to composite advancement. When fillers are added to composites made from high-k polymer systems, the leakage current and dielectric loss of such materials rise; finally, the vast disparity in permittivity causes the electric field within the composites to be distorted when subjected to an external electric field. There are different polymer blenders and polymer composites which showed high-k dielectric constant are discussed below.

Polymer–Polymer Blends and Composites for High-*k* Dielectric Properties

Dang investigated a PP/PVDF blend, which stands for polypropylene/polyvinylidene fluoride [37]. Novel high PVDF is combined with PP matrix to increase permittivity. Permittivity reached ~5.4 at 1000 Hz, approximately 3 times pure PP's (~2.2). This blended solution combines the dielectric characteristics of PVDF with the processability of polymers. They might offer a new generation of capacitor dielectric films. Using solution mixing and casting, polymer blend films were made. This film's 100 Hz permittivity is 12. This is higher than PMMA (~2.9) and nears PVDF.

Nan et al. explained the combined ArPTU with PVDF for solution-cast composite films for dielectric application [38]. Permittivity and dielectric loss at 1 kHz are 9.2 and 0.02. Blend films restrict early polarization saturation at low fields, improving breakdown strength and energy density. PVDF/ArPTU (90/10) film has 10.8 J/cm^3 energy density at 700 MV/m and 83% charge–discharge efficiency. At certain volume fractions, the permittivity of polyvinylidene fluoride-polyamide (PA11)/PVDF blends can approach 60, which is twelve times greater than PA11 (~5) alone and five times higher than PVDF (~12). Dielectric permittivity (k_{blend}) surpassed those of the constituent polymers, unlike ordinary polymer blends [39]. These findings show that polymer-blended systems with high-permittivity components are a new, versatile, easy-to-process material. They may be used in flexible electronics.

For low-loss, high-energy-density capacitors, Zhang et al. suggested polar-fluoropolymer blends with tailed nanostructures [40]. Poly(ethylene-chlorotrifluoroethylene) [P(VDF-CTFE)] and poly(vinylidene fluoride-chlorotrifluoroethylene) [P(VDF-CTFE)] are two examples of such mixes (ECTFE). Classical composite theory predicts a dielectric constant of 7 and modest loss (~1%) for blend and cross-linked blend films. Cross-linking blends increased nanoscale mixing, reducing losses in blend films at high fields while preserving energy density.

6.4.6 Ceramic and Polymer-Ceramic Composites as Dielectric Materials for High-k *and Low-*k *Dielectric Applications*

Linear or nonlinear dielectric materials exist. An electric field induces polarization in linear dielectrics, and removing it depolarizes the material. There is a subcategory for both polar and nonpolar substances. Polar molecules retain their dipole moments even when exposed to no external electric field. Generally speaking, the dipole moments of molecules in polar dielectrics are larger when they are not symmetric. They experience electronic and ionic polarization, making them molecules without permanent dipole moments. Alkali halides, metal oxides, paraffin, benzene, and carbon chlorides are all examples of ionic crystals. Molecules in nonpolar dielectrics do not exhibit a persistent dipole–dipole moment because of the symmetry between the positive and negative charges. External fields cause them to become polarized.
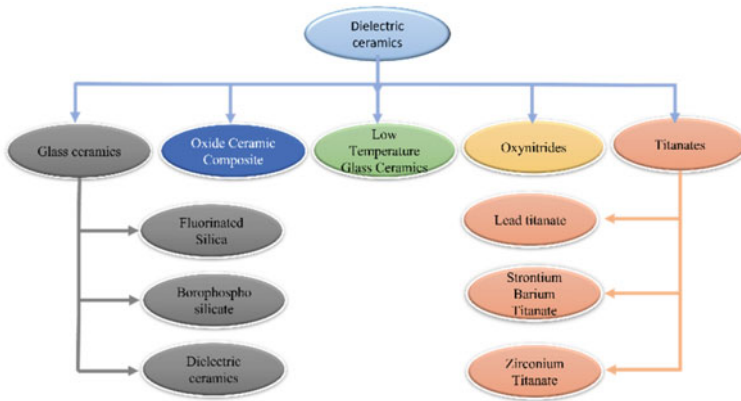
Fig. 6.10 Classification of dielectric ceramic materials

When it comes to polar molecules, atoms or molecules with spherical symmetry have their electron clouds pointing in the direction of the electric field. Positive and negative charges are generated via polarization. These materials include atoms or molecules such as silicon, as well as inert gases, liquids, and solids. These chemicals are polarized by electrons. Ceramics are composed of inorganic, nonmetallic, and nonorganic components, as seen in Fig. 6.10. Heat processing is possible with single or polycrystalline ceramics. Ceramics are corrosion-resistant while remaining stiff and brittle. Because new technologies do not need traditional ceramic compounds, better ceramics have been developed to keep up. Despite its mechanical shortcomings, ceramics have a high stiffness factor, hardness, and abrasion resistance. They are resistant to corrosion and heat. Modern ceramics are employed in the electrical industry due to their material properties. Ceramics are resistant to both weather and electricity. Ceramics are used in the electrical and engineering industries because of their properties. Advanced ceramics that are often used include aluminum oxides and zirconium oxides. Carbides, nitrides, silicides, and borides are examples of ceramics that are not oxides. Single-crystal silicates are used in high-capacity capacitors, whereas steatite tubes are characterized by low permittivity and capacitance. The high permittivity of titanium oxide led to the development of ultracapacitors.

6.4.6.1 Glass–Ceramic

Some of us may be aware that sand from the soil is heated and melted to create glass. The amorphous compounds of silicon and lime make up glasses. Glasses made from soda-lime and silicate are rather common. Despite their names, soda-lime and silicate glass–ceramics do not include any of the aforementioned elements. Pure silicate and borate glasses have a 3.2 to 3.8 MHz dielectric constant. Even though the composites have a higher dielectric permittivity than pure borates and silicates, their

values are still below 4.2, making them low-k dielectric ceramics. The dielectric constant might be increased to more than 4.2 with the help of certain 'dopants. Alumina doping helps ceramics attain 5 and 1 MHz permittivity. Lead borosilicate glass (~7.0), magnesium aluminosilicate glass (~5.0), calcium aluminosilicate glass (~6.0), and lithium silicate glass (~6.5) have low permittivity as compared to others. Glass–ceramics have high dielectric constants and thermal expansion coefficients, making them ideal for multilayer ceramics. High-performance packaging and pin grid arrays employ these chemicals [41].

Borosilicate glass has a dielectric constant between 3.9 and 4.2, placing it in the family of low-*k* dielectrics with two other amorphous phases. The matrix was formed at 950 °C, matching silica's thermal expansion coefficient. Extra dopants are needed to prevent silica matrix martensitic transformation. Pure silica has a permittivity of 4 and is the inorganic limit. Porosity and how porous channels increase dielectric characteristics have been studied in this substance [42]. Polymers are included in these silica matrices. Polymer-modified ceramics fulfill low permittivity and losses. Molecular clusters may be seen in microscopic examinations of silica and polymer-modified silica gels. In order to create nanopores, a two-phase technique is required, consisting of a continuous solid phase and a porous air phase.

Connection in ULSI circuits, including computer DRAM chips, MPUs, and application-specific ICs, requires multilayer dielectric thin films. Therefore, the dielectric permittivity of these layers should be kept low to minimize signal latency and cross talk. Fluorinating silica matrices is one approach to reducing dielectric permittivity. Silicon oxide-fluoride films are formed on silicon via chemical vapor deposition (CVD) [43].

Borophosphosilicate (B_2O_3–P_2O_5–SiO_2) ceramic glass is a good electronic packaging material. With their glass–ceramic composition, boron trioxide and phosphorous pentoxide boost the coefficients. The 1:1:2 stoichiometric ratios characterize these glass–ceramics dielectric constant and loss tangent. Glass-derived ceramics internalize these chemicals. Additional sintering and surface crystallization yields external nucleation in these composites, and the use of silver, gold, and copper in metallization indicates the viability of tape casting for fabricating multilayer glass–ceramic sheets. Borophosphosilicate glass–ceramics made by heating fine-grained boron phosphate glass–ceramics. Silica renders the composite acid, basic, and water-resistant. Sol-gel synthesis includes introducing reagents at the correct temperature and pressure in an alkaline environment. Boron (tetramethyl borate), phosphorus (tetramethylphosphite), and modified silica (tetramethylorthosilicate) alkoxides are used. (Tetramethoxysilane will also be utilized as a catalyst) [44].

6.4.6.2 Oxide Composites of Glass–Ceramic

To create samples with low permittivity and optimum thermal expansion coefficients, dielectric interlayers mix cordierite, quartz, and borosilicate substrates. This oxide glass–ceramic is used in high-temperature ceramic filters, structural ceramics, and

solid oxide fuel cells. Ceramic fillers include bismuth, silica, alumina, and magnesium oxides. Impedance analyzer dielectric constants are 8.8–9.04 at 13.4 GHz. The calcium titanate powder dielectric resonator is sintered for 4 h at 1450 °C at 6.55 GHz, and dielectric permittivity was 40.5–20.7 [45]. It has been shown that oxides of ceramic-glass composites, such as bismuth, sodium, potassium, and titanates, all contribute to better energy storage. High sintering temperatures and sintering aids maximize microwave ceramics. These aids may boost permittivity and thermal expansion. Discontinuous and increased grain development in oxide ceramics reduce performance. To prevent holes and discontinuous grain development, chemicals and many precautions are utilized.

6.4.7 Dielectric Perovskite and Dielectric Polymer-Perovskite Composite Materials

Due to the fact that electro-ceramics may be made from more than 3000 different compounds, perovskites have drawn particular interest in the field of dielectrics for microwave communication. Perovskites are one of the few ceramics that enable applications demanding optimal dielectric characteristics and low TCF values, making them a promising candidate for use as microwave dielectrics for wireless communication. There are five distinct lattice configurations in which the simple perovskite structures may be found: the cubic, tetragonal, hexagonal, orthorhombic, and rhombohedral structures. The structure of these influences the operating temperatures in microwave devices, and each of them has a distinct transition for providing paraelectricity [46].

Common structures in low-cost perovskite electronics include A-titanate, A-zirconate, and R-BO3. These crystals have a non-perovskite structure with a high packing factor and include a, B, and R as substitutes for barium, calcium, aluminum, strontium, magnesium, and zinc. They are straightforward perovskite ceramics, thanks to the chemicals in their metal oxide composite. In addition, the addition of rare earth metals like neodymium and lanthanum, which are stoichiometrically regulated, results in modified perovskite ceramics with specific uses. In recent years, a barium magnesium and tantalum (BMT) composite has shown to be an effective hexagonal perovskite, thanks to its stable temperature and optimum temperature coefficients. Dopants like niobium and manganese may be used to dope BMTs, which have high dielectric characteristics (permittivity of 25 at 10 GHz) and a TCF of 2.7 ppm/K. It was also proposed that at high sintering temperatures of 1650 °C, this might be difficult for commercial application since defects in the material would be introduced [47].

6.4.8   Dielectric Rare-Earth and Polymer-Rare Earth Composite Materials

Since lead-free ceramics ($BaTiO_3$) are not dangerous to people or the environment, they are particularly popular in the electronics sector. Due to its exceptional electrical characteristics, high permittivity, and use in cutting-edge electrical appliances, rare earth (RA)-doped barium titanate ($BaTiO_3$) has had its dielectric properties examined. Here, research on the dielectric properties of $BaTiO_3$ ceramics doped with RA (lanthanum (La), erbium (Er), neodymium (Nd), samarium (Sm), and cerium (Ce)) was described. The primary goal of this review is to investigate the effects of doping on the described RA's $BaTiO_3$'s dielectric characteristics.

6.4.9   Carbon and Polymer-Carbon-Based Composite Materials for High- and Low-k Dielectric Application

High-*k* dielectric polymer composites may be made by combining carbon nanostructures with polymers. Despite their low percolation threshold, nanocomposites have high permittivity. Polymers are the first step. Practical applications are limited by the high dielectric loss and low breakdown field. The biggest challenge is resolving conflicts. Carbon-based compounds may improve the dielectric characteristics of polymers. Table 6.4 summarizes some polymer-carbon composite studies for high dielectric applications. Carbon nanotubes and graphene have the potential to improve the dielectric properties of dielectric polymers at low concentrations while maintaining composite flexibility [52]. High electrical conductivity and significant dielectric loss are possible near percolation when conductive particles tunnel. Composites are unable to endure electric fields over the percolation threshold. This flaw hampered the formation of conductive high-*k* composites. It is critical to raise the dielectric constant while lowering dielectric loss and composite flexibility. Carbon additions improve matrix polymers mechanically and electrically. Graphite, carbon fiber, CNTs, graphene, and reduced graphene oxide are examples of carbon fillers. According to experts, polymer-carbon nanocomposites have a variety of uses. Carbon improves the electrical and mechanical characteristics of polymers. Carbon-containing polymer composites have received a lot of attention. Carbon comes in a variety of shapes, sizes, and characteristics. The enormous surface area of carbon strengthens composites. Under mild stress, carbon nanotubes increase their mechanical and electrical qualities. CNTs benefit from a high aspect ratio.

Filler geometry, size, surface area, physical and chemical properties, interfacial interactions with the matrix-polymer, filler–filler interactions, filler concentration, mixing method, temperature, shear effects, composite morphology, and operating frequency can all have an impact on the dielectric properties of polymer-carbon composites [53]. It is possible to use one-, two-, or three-dimensional composite fillings. Thanks to their excellent functional and structural features,

Table 6.4 Rare-earth-doped ceramics dielectric properties

$Ba_{1-x}La_{2x/3}TiO_3$	Curie temp. (K)	Permittivity	Ref.	$Ba_{1-x}Sm_{2x/3}TiO_3$	Curie temp. (K)	Permittivity		Ref.
X = 0.00	390	5900	[48]	X = 0.00	390	5800		[49]
X = 0.02	353	4600		X = 0.02	373	5200		
X = 0.04	318	6500		X = 0.04	353	7000		
X = 0.06	293	9100		X = 0.06	343	7400		
X = 0.08	230	8600		$Ba_{1-x}Ce_xTiO_3$	Curie temp (K)	Permittivity		Ref.
$Ba_{1-x}Er_xTiO_3$	Curie temp (K)	Permittivity	Ref.	X = 0.00	110	1000		[50]
X = 0.00	133	5350	[51]	X = 0.01	100	2050		
X = 0.01	133	19,606		X = 0.01	100	5050		

Table 6.5 Polymer-carbon-based dielectric materials and its properties

Composites	Dielectric constant	Dielectric loss	Refs.
PAni/rGO	51.8	0.0093	[54]
PAni/rGO/BaTiO$_2$	54	7.83	[55]
PVDF/CNT	39	87	[56]
PVA/GA	70	0.9	[57]
CNT/GNP	41	0.9	[57]

carbonaceous nanofillers like CNTs and graphene play a crucial role. Table 6.5 showed some polymer-carbon-based dielectric material properties that are highly useful for optoelectronic applications.

6.4.10 Negative Permittivity Polymer Composites

There has been a lot of research on the positive permittivity of dielectric composites over the years; however, certain met composites, because of their unusual electromagnetic properties, may generate a negative permittivity. Negative permittivity from metallic wire arrays and electric fields provide negative permeability in epsilon-negative materials (ENMs). Theoretically, applied voltage and ENM current follow a new dielectric theory basic. They are mostly used in electronic packaging as interference shields or insulators between layers of dielectric composites. This fitting approach improves space-charge polarization owing to two heterogeneous interfaces. New literature reviews ENM-promising polymer-based composites. A nickel-rutile cermet negative permittivity metamaterial was explored in liquid–solid

structure compounds. The conduction mechanism shifted from hopping to metallic when nickel concentration increased in percolative cermet. The magnetic behavior of the epsilon-negative cermet was less than 1, confirming that conductive networks caused a high-frequency diamagnetic response of eddy currents [58]. After sintering, indium oxide-doped ceramics were studied for negative permittivity. The negative permittivity seen during monophase indium-tin-oxide sintering was traced back to an increase in the concentration of charge carriers, as predicted by the Drude–Lorentz oscillator model. The dielectric properties were influenced by the presence of free carriers [59].

Negative permittivity metamaterials with "bilayers" have been created to find the frequency zones with the greatest and lowest dielectric permittivity. Wang et al. (2016) discovered that permittivity increased by 40% while dielectric loss remained at 0.06. (considered low at relaxation frequencies). The author also showed thickness ratio and single-layer composites versus dielectric characteristics [60].

For the purpose of studying diamagnetic ENMs, Engheta et al. [61] recommended using a narrow subwavelength cavity dielectric resonator constructed from metamaterials with negative permittivity and permeability. This discovery is important, as metamaterial-based composite production uses mathematical procedures [61]. After this investigation, a laminated composite with a negative permittivity intermediate layer was investigated to increase its permittivity. Wang et al. [62] found that strong interfacial polarization and low-loss tangent owing to the ohmic barrier effect increased permittivity. Table 6.6 showed some examples of negative polymeric composites that showed a negative dielectric constant.

6.5 Summary

This chapter provides a comprehensive examination of dielectric materials, highlighting their enormous variety in terms of both materials and manufacture. The majority of the materials included in this study are ceramics, metals (oxide, sulfide, and nitride), carbon-based materials, and polymers, which provide a clear distinction between their uses for energy storage, insulation, energy storage, and power transmission due to their dielectric properties. Both low-permittivity and high-permittivity materials that may be used in a variety of applications are distinguished by the materials discussed above.

There is great potential in the development of hybrid polymer composites that include natural fiber reinforcement, and it is essential that researchers learn how to optimize their characteristics for use in industry. These composites have the potential to be employed as intrinsically conductive polymers (ICPs) in the semiconductor industry; nevertheless, lowering the material's high contact resistance remains a challenge. When a change in pressure or temperature is given to a functional model, hybrid polymer composites are created to simplify the flow of electricity in ICPs and maximize load transfers. Dielectric constants must be nominal for proper charge

Table 6.6 Dielectric characteristics of epsilon-negative polymeric composites

Composites	Filler materials	Dielectric loss	Dielectric constant	Refs.
Ti_3AlC_2-polyimide	Ti_3AlC_2	0.1–100 (between 10 MHz and 1 GHz)	−1200 toward 0 (between 10 MHz and 1 GHz)	[63]
Graphene/ polyvinylidene fluoride	Single-layer graphene	0.1 lowest and 1 M highest (between 200 kHz and 1 MHz)	−7250 constant (between 200 kHz and 1 MHz)	[64]
Polydimethylsiloxane/ multi-walled carbon nanotubes (PDMS/ MWCNTs)	Membranous metacomposite	0.01–100 (between 10 MHz and 1 GHz)	300 toward −20 @ 933 MHz (between 10 MHz and 1 GHz)	[65]
Flexible graphene/ PDMS metacomposite	Flexible graphene addition	–	−61,250 toward − 40,855 (between 10 kHz and 1 MHz	[66]
MWCNT/TiN/CCTO	Sintered in argon and nitrogen	1000 to 100 (between 93 and 683 MHz)	−200 max (between 93 and 683 MHz)	[67]
Ag/Al$_2$O$_3$/3D-BaTiO3/ epoxy	Silver-conductive particles	0.02 toward 10 (between 10 kHz and 1 MHz)	−4 M toward 0 (between 10 kHz and 1 MHz)	[68]

export, and dielectric losses must be reduced to avoid the leakage of undesired charges that might harm the composite material at the working temperature.

Even though ceramics have excellent dielectric properties, they cannot be used in current applications due to their high production temperature, high cost, and low mechanical strength. The great electrical performance of polymers and their composite combinations make them good material for use in integrated circuits and multilayer dielectric printed circuit boards. In an electric field, polymer composites undergo polarization processes that give them a high dielectric constant while exhibiting little dielectric loss, similar to ceramic composites. Fiber-reinforced polymer composites (FRP) are a kind of polymer composite that may be used for specific purposes that might impact the cost, processing power, green material usage, and waste management of energy storage and insulation systems.

Conflict of Interest The authors confirm that there are no personal or professional conflicts of interest that may be seen as influencing the findings given in this chapter.

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