Fundamentals, processes and applications of high-permittivity polymer–matrix composites

Zhi-Min Dang, Jin-Kai Yuan, Jun-Wei Zha, Tao Zhou, Sheng-Tao Li, Guo-Hua Hu

**ABSTRACT**

There is an increasing need for high-permittivity (high-k) materials due to rapid development of electrical/electronic industry. It is well-known that single composition materials cannot meet the high-k need. The combination of dissimilar materials is expected to be an effective way to fabricate composites with high-k, especial...
for high-k polymer–matrix composites (PMC). This review paper focuses on the important role and challenges of high-k PMC in new technologies. The use of different materials in the PMC creates interfaces which have a crucial effect on final dielectric properties. Therefore it is necessary to understand dielectric properties and processing need before the high-k PMC can be made and applied commercially. Theoretical models for increasing dielectric permittivity are summarized and are used to explain the behavior of dielectric properties. The effects of fillers, fabrication processes and the nature of the interfaces between fillers and polymers are discussed. Potential applications of high-k PMC are also discussed.

© 2011 Elsevier Ltd. All rights reserved.

Contents

1. Introduction ..................................................................... 662
2. Fundamental aspects of high-k composites ................................ 665
   2.1. Definition of high permittivity (high-k). ................................ 665
   2.2. Capacitance and electric energy storage of materials .................. 666
   2.3. Polarization and relaxation of dielectric materials .................... 666
   2.4. Dielectric strength of random polymer–matrix composites ............. 668
   2.5. Theoretical models for dielectric properties of polymer–matrix composites ............. 669
      2.5.1. Maxwell–Garnett equation ............................................. 669
      2.5.2. Bruggeman self-consistent effective medium approximation ............ 670
      2.5.3. Jaysundere–Smith equation ............................................. 670
      2.5.4. Lichtenker rule ......................................................... 671
      2.5.5. Percolation model ....................................................... 671
   2.6. Connection type of PMC ................................................... 674
3. Processes for the fabrication of high-k PMC ................................ 674
   3.1. Solid phase processes ....................................................... 674
      3.1.1. Direct compounding ...................................................... 674
      3.1.2. Melt compounding ...................................................... 675
   3.2. Liquid phase processes ..................................................... 675
      3.2.1. Liquid-phase assisted dispersion ..................................... 675
      3.2.2. Solution route .......................................................... 676
   3.3. In situ polymerization processes ........................................... 676
4. Microstructure and interfaces of high-k PMC ................................ 677
   4.1. Two-phase high-k PMC ..................................................... 677
   4.2. Three-phase high-k PMC .................................................. 681
5. Effect of fillers on dielectric properties of high-k PMC ..................... 683
   5.1. Concentration effect of fillers on dielectric properties ................... 684
      5.1.1. Effect of ceramic fillers ............................................... 684
      5.1.2. Effect of electrical conducting fillers .................................. 687
   5.2. Size effect of fillers on dielectric properties of PMC ................. 689
      5.2.1. Change in physical properties of fillers with size reduction ............ 689
      5.2.2. Dependence of dielectric properties of PMC on size of fillers .......... 690
      5.2.3. Effect of micro–nanosize cofillers on dielectric properties of PMC ........ 692
   5.3. Shape effect of fillers on dielectric properties ............................ 694
      5.3.1. Shape of fillers and filler–polymer connectivity ..................... 694
      5.3.2. Effect of 1-dimensional fiber-shape fillers on dielectric properties ........ 695
      5.3.3. Effect of 2-dimension plate-shape fillers on dielectric properties .......... 698
      5.3.4. Effect of core–shell fillers on dielectric properties .................. 698
6. Effects of measurement conditions on dielectric properties ............. 700
   6.1. Temperature dependence of dielectric properties ...................... 700
      6.1.1. Organic fillers/polymer composites ................................ 700
      6.1.2. Insulating ceramic fillers/polymer composites ...................... 701
1. Introduction

As predicted by Moore’s law, the efficiency of electronic products is improving in an exponential manner [1,2]. This rapid improvement in efficiency is concomitant with the creation of new materials with high permittivity (called high-\(k\) dielectric materials). A higher-\(k\) dielectric material can store more electric energy than a lower one. As a result, its use in electronic devices allows improving their efficiency. Electronic systems are often composed of active components such as integrate circuits (ICs) and passive components. Passive components have become of an increasing interest because they are steadily growing in number as the electronics industry is progressing toward higher functionality [1]. For example, the ratio of the passive to active components in a mobile cellular phone is over 20 [2]. In the next generation packaging technology, the passive components such as capacitors (C), resistors (R) and inductors (L) will be integrated into the substrate as a thin film layer instead of being surface mounted on the top of the substrate as discrete components. The passive components buried inside the substrate are called integral passives or embedded ones. Embedded passives provide many advantages over discrete components and play an important role in microelectronic field, as shown in Fig. 1 [3].

Among all passive components, capacitors call for special attention. Fig. 2 shows the market shares of capacitors, resistors, and inductors in the United States. Because of the large amount of capacitors employed in electronic systems, integration of capacitors is of much importance. Capacitors have many applications, as shown in Table 1. They can be used for filtering, timing, alternating/direct (A/D) current conversion, termination, decoupling, and energy storage. Particularly, the development of microelectronics requires decoupling capacitors with higher capacitance and shorter distance from its serving devices [4].

Apart from electronic industry, high-\(k\) materials are widely used in many civilian and military applications including active vibration control, aerospace, underwater navigation and surveillance, hydrophones, biomedical imaging, non-destructive testing and air imaging microphones [5,6]. For example, high-\(k\) elastic rubber–matrix composites could be used as potential functional materials for cable accessories in electrical engineering because they could balance the distribution of electric field of cable terminal to prevent the cable from failure. Fig. 3 shows a clear field distribution of cable terminal before and after the use of high-\(k\) rubber–matrix materials.

In fact, ceramics and metals with high stiffness and excellent thermal stability have also a high-\(k\). However, their high density, brittleness and challenging processing conditions impede their use as high-\(k\) materials. On the other hand, polymers have the advantage of easy processing and mechanical flexibility and low cost. Moreover, integration of resistors and capacitors into the internal structure of printed wiring boards (PWB), or, directly into integrated circuits packaging requires materials compatible with polymers used as support of electronic circuits [7–10]. Mechanical flexibility and tunable properties of polymer matrix composites (PMC) make them attractive. In addition, polymer materials
have found many applications for electromechanical devices to perform energy conversion between the electric and mechanical forms. These devices could be served as artificial muscles, smart skins for drag reduction, actuators for active noise and vibration controls, and microfluidic systems for drug delivery and micro-reactors [11–14]. However compared with inorganic materials, organic polymer materials have often low dielectric permittivity, in the range of 2–5 [15]. In exceptional cases the dielectric permittivity of a pure polymer can go beyond 10, but is still very low, impeding their use for high-\(k\) applications, despite their excellent physical properties. Thus a key issue is to substantially raise the dielectric permittivity of polymers while retaining their excellent mechanical properties. Very recently, polymer composites with high-\(k\) and low dielectric loss and good process compatibility

![Fig. 1. (a) Technology trend and market for organic substrates, (b) a schematic image of embedded passive substrate, the arrow showing position of passives [3].](image1)

![Fig. 2. Market share of capacitors, resistors, and inductors [4].](image2)

**Table 1**

<table>
<thead>
<tr>
<th>Application</th>
<th>Value range</th>
<th>Stability required</th>
<th>Tolerance required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtering, timing</td>
<td>1 pF to 100 nF</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>A/D Conversion</td>
<td>1 pF to 10 nF</td>
<td>Very high</td>
<td>Very high</td>
</tr>
<tr>
<td>Termination</td>
<td>50–200 pF</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Decoupling</td>
<td>1–100 nF</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Energy storage</td>
<td>&gt;1 (\mu)F</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>
with printed circuit boards (PCBs) have been recognized as promising candidate dielectric materials for embedded capacitors. This is because high-$k$ polymer composites provide an ideal solution to combine the dielectric and electrical properties of the ceramic or metal fillers and the low-temperature processability and mechanical properties of the polymer matrix [16–45]. Furthermore, their good adhesive properties are additional advantage for their use in embedded capacitor technology, which pure ceramics or other dielectric materials lack.

Recently, a few strategies, including random composites of polymers, field structured composites and synthesis of new polymers, have been developed to improve the dielectric permittivity of PMC. The most common one is addition of fillers in polymers to make composites. These fillers includes metals [16–25], ceramics [26–45], carbon based materials [46–62] and organic fillers such as semiconductor oligomer [63–71] and conducting polymers [72–76]. In general, ceramic–polymer composites are prepared by adding high-$k$ ceramic fillers in polymer matrices [26–45]. The advantages of these composites include predictable dielectric properties, relatively low dielectric loss and easy fabrication [20,28,29,43]. However, remarkable issues for use of the ceramic–polymer composites are related to the deterioration of mechanical and processing properties due to the high concentration of rigid ceramic particles in the flexible polymer matrix. By replacing ceramic particles with conductive particles, percolative polymer composites can be made with a drastic increase in dielectric permittivity in the vicinity of the percolation threshold of the conductive particles. For example, high-$k$ dielectric composites with highly conducting fillers such as metals and carbon nanotubes have been developed on the basis of percolation [16–25,63–76]. A permittivity value of 2000 has been reported for silver flakes-doped epoxy systems [77]. Dang et al. reported a value of 400 in Ni/PVDF composites [19,20]. These remarkable increases in dielectric permittivity, however, are always concomitant with significant increases in electrical conductivity and dielectric loss due to the ‘insulator–conductor’ transition occurring at the percolation threshold. This transition also leads to extreme sensitivity of the dielectric permittivity to the content of the conductive fillers. In other words, a small deviation from the percolation threshold could result in serious drop of the dielectric permittivity, making it rather difficult to control the parameters of the preparation process. The issues mentioned above are considered as drawbacks for conducting fillers/polymer composite systems.

As a milestone, superior electrical properties of nanotubes offer exciting opportunities for new high-$k$ polymer composites. Apart from electrical properties, nanotubes also impart better mechanical properties to composites at relatively low filler content [52]. Higher surface area and larger aspect ratios are responsible for superior dielectric properties of nanotube composites [50,51]. At the same time, agglomeration of nanotubes and their compatibility to polymer matrices are prime concern of researchers in this field. Although different strategies including modifications of nanotubes are employed, it is yet difficult to fully overcome these challenges [78]. All-organic composites based on conducting organic fillers such as conducting polymers are a new and interesting field in high-$k$ dielectric composites. This type of filler has the advantage of increasing the dielectric permittivity of host polymers without much deterioration of their mechanical properties. Zhang et al. have developed a number of high-$k$ polymer composites using organic semiconducting fillers [64]. Other types of fillers can also
be used in these polymer composite systems to achieve required electrical and mechanical properties. These types of composites are termed as three-phase polymer composite systems [20,44,54,57,59,61,65]. Apart from fillers, different types of polymer matrices are also used. Choice of polymer matrix depends upon the type of application of the final product. Thermoplastic, thermoset [23,33,38,43,45] and elastomer [56,61] are all good candidates as hosts to high-k polymer composites.

Dielectric permittivity of composites depends on the filler concentration. In the case of dielectric fillers with low conductivity, such as ferroelectric ceramics and organic fillers, an increase in dielectric permittivity of composite with respect to the filler concentration can be explained by well established laws such as Bruggeman self-consistent effective medium approximation [79,80], Maxwell–Garnett equation [80,81], Lichtenker rule [82], Jaysundere and Smith (J–S equation) [83] models. Compared to ceramic–polymer composite systems, a percolative behavior is observed in the case of high conducting fillers. In these percolative composites, high dielectric permittivity up to 1000 can be achieved in the vicinity of the percolation threshold. An increase in dielectric permittivity of composites in the vicinity of the percolation threshold can be explained by the well-known power law. It is widely believed that in the case of a percolative system, ultra-high dielectric permittivity of composites is not a direct consequence of intrinsic dielectric permittivity value of fillers and host polymer as in the case of ceramic–polymer composites. It is often considered as a consequence of interfacial polarization and an effective increase of electrode surface area due to interconnection of conductive particle clusters near the percolation threshold [80,84]. In other words, interfaces between polymer and filler are very important in these percolative systems. They can be tailored by a number of variables. They include the type and level of reinforcement, size and shape of filler, the type of matrix, and the composite preparation process. All these factors are inter-related and should be considered systematically when developing a new material with high-k. Other parameters like temperature and electric field also have an effect on dielectric properties of polymer composites.

This paper attempts to review the development in the field of high-k polymer matrix composites and provide a systematic and comprehensive analysis of the fundamental aspects of high-k flexible materials and their potential applications. It is organized as follows. In Section 2, fundamentals relative to dielectric permittivity are introduced. They help to understand the characteristics of dielectric properties of composite materials. Section 3 discusses fabrication processes for high-k PMC. In Section 4, the effects of microstructure and interfaces of high-k PMC on dielectric properties are addressed. Other factors affecting the dielectric properties of high-k PMC are discussed in Sections 5 and 6. Section 7 presents potential applications and unsolved issues of high-k PMC in different fields. This paper ends up with concluding remarks and future perspectives.

It should be mentioned that this review paper does not intend to cover all aspects of high-k PMC and related topics, due mainly to the rapid growth of this field and space limitations. The concluding remarks and perspectives only reveal the authors’ own viewpoint. We apologize in advance for any glaring omissions of pertinent works related to the topic of this paper. Of course, any technical deficiencies in this paper are our own.

2. Fundamental aspects of high-k composites

2.1. Definition of high permittivity (high-k)

The term high-k dielectric refers to a material with a high dielectric permittivity (k) as compared to SiO₂ used in semiconductor manufacturing processes. The use of high-k materials has extended beyond electronics and has triggered the development of other high-k materials including PMC. Although high-k PMC cannot be considered as gate dielectrics due to some well-known disadvantages, they could be applied in other electronic devices. Moreover, their mechanical flexibility and tunable properties make them appealing for high-k materials. It should be pointed out that the symbol ‘k’ for dielectric permittivity is mostly used in the microelectronic field. In electrical engineering and other fields, the symbol ‘ε’ is commonly employed. In this review paper, the symbol ‘k’ is used throughout.
2.2. Capacitance and electric energy storage of materials

Two conducting electrodes separated by a dielectric constitute a capacitor (formerly called a condenser). If a battery of potential difference \( V \) is connected across the electrodes then the capacitor can store electric charge \( Q \), expressed in coulombs, that is directly proportional to the applied voltage, expressed in volts \( V \), according to the following equation:

\[
Q = CV
\]

where \( C \) is the capacitance expressed in farad (F). Hence the capacitance value is defined as 1 F when the electric potential difference across the capacitor is 1 V, and a charging current of 1 A flowing for 1 s. The farad is a very large unit and is not encountered in practice. Therefore submultiples of the farad are commonly encountered. In decreasing order of use, they are the picofarad (pF), the nanofarad (nF), and the microfarad (mF). The capacitance of a capacitor with parallel electrodes is directly proportional to the active electrode area and inversely proportional to the dielectric thickness as described by the following equation:

\[
C = k_0 k_r \frac{A}{d}
\]

where \( k_0 \) is the dielectric permittivity in vacuum and is 8.854 pF/m, \( k_r \) is the relative permittivity. The latter is a dimensionless physical quantity equal to the ratio of the permittivity of the medium to that in vacuum. If the medium is a macroscopical material, it is often called the dielectric constant of the material. Hence the dielectric permittivity \( k \) is defined by the equation \( k = k_0 k_r \). Eq. (1) shows when an electric field is applied to a capacitive material; electric energy can be stored in it.

2.3. Polarization and relaxation of dielectric materials

In general, the permittivity of an insulating material depends on the frequency \( \nu \) in Hertz (Hz) of the applied electric field and can be described as a complex physical quantity, where the imaginary part is related to dielectric loss. The frequency dependence reflects the possible existence of dispersive behaviors somewhere in the electromagnetic spectrum. The relative dielectric permittivity is a frequency dependent complex quantity.

\[
k' \left( \omega \right) = k' \left( \omega \right) + jk'' \left( \omega \right)
\]

where \( \omega \) is angular frequency and \( \omega = 2\pi\nu \), \( k'(\omega) \) denotes the real part of dielectric permittivity and \( k''(\omega) \), the imaginary part. Usually the dielectric permittivities of materials listed in databases are measured at a frequency of 1 MHz unless otherwise specified. The real part \( k' \) is always different from zero and represents the contribution to the polarization responsible for the energy storage in the material. In order to address its substantial independence from the electric field, it is often referred to as the relative dielectric permittivity of a material. The imaginary part \( k'' \), usually called loss factor, shows possible dissipative effects and its frequency spectrum differs from zero only in dispersive regions. Sometimes, the dissipative behavior is characterized by means of the so-called loss tangent, which is defined as \( \tan \delta(\nu) = k''(\nu)/k'(\nu) \).

In a homogeneous material, the polarization and thus \( k'(\omega) \) result from various contributions. The latter add up to give an effective relative complex dielectric permittivity \( k_{\text{eff}} \), which may be defined in a very general form as follows:

\[
k_{\text{eff}} = k' \left( \omega \right) + \sum_i k_{\text{MW,i}} \left( \omega \right) + j \left( \frac{\sigma_{\text{DC}}}{\omega k_0} \right) = \left( k' \left( \omega \right) + \sum_i k_{\text{MW,i}} \left( \omega \right) \right) + j \left( k'' \left( \omega \right) + \sum_i k_{\text{MW,i}}'' \left( \omega \right) + \frac{\sigma_{\text{DC}}}{k_0} \right)
\]

where \( k_{\text{MW,i}} \) accounts for the \( i \)th interfacial contribution and \( \sigma_{\text{DC}} \) is direct current (DC) electrical conductivity. It is worth noting that all the dispersive phenomena associated with the intrinsic polarization are accounted for by \( k' \left( \omega \right) \) in Eq. (4). In the presence of multiple intrinsic relaxation, \( k' \left( \omega \right) \) can be
expressed as a superposition of individual contributions. Indeed, each relaxation process, either orientational or interfacial, can be analytically described by means of a proper relaxation function. In the simplest case of a material consisting of identical and non-interacting dipoles and whose relaxation is characterized by a unique time constant $\tau$, Debye derived a relaxation function for the complex permittivity in the associated dispersion region [79,80]. In the frequency domain, the Debye model gives the well-known formula:

$$k'(\omega) = k_\infty + \frac{k_s - k_\infty}{1 + j\omega\tau}$$  \hspace{1cm} (5)

where $k_s$ and $k_\infty$ represent, respectively, the static (relaxed) and the high frequency (unrelaxed) values of the permittivity with respect to the considered process. For a material showing a unique dipolar relaxation in its whole spectrum, $k_\infty$ in turn coincides with the aforementioned relaxed value of the deformational permittivity. Eq. (5) can be split into its real and imaginary parts and then equivalently expressed by the following pair of equations:

$$k'(\omega) = k_\infty + \frac{k_s - k_\infty}{1 + \omega^2\tau^2}$$  \hspace{1cm} (6a)

$$k''(\omega) = \frac{(k_s - k_\infty)\omega\tau}{1 + \omega^2\tau^2}$$  \hspace{1cm} (6b)

Due to the very simplistic assumptions above, the Debye model fails in describing relaxation phenomena in complex systems. Thus, Havriliak et al. proposed a more general formula using a phenomenological approach [79,80]. It has the merit of including the possibility of a distribution of different time constants through the introduction in Eq. (6a) of two shape parameters $\alpha$ and $\beta$:

$$k'(\omega) = k_\infty + \frac{(k_s - k_\infty)}{1 + (j\omega\tau)^1-\alpha}$$  \hspace{1cm} (0 < \alpha < 1, \hspace{0.5cm} 0 < \beta < 1)$$  \hspace{1cm} (7)

Actually, the occurrence of a dispersive process of any nature in the frequency region of interest represents a drawback. In order to advantageously exploit the application of a dielectric material, the effective loss factor should be kept as low as possible. In fact, losses not only waste part of the input energy, but also worsen the insulation properties of the materials. In particular, for any dielectric material it is possible to identify a threshold electric field, which generates irreversible modifications in the medium accompanied by the onset of an intense and disruptive flow of charges. Such a sudden loss of insulation due to a very high electric field is called dielectric breakdown of the material. The minimum field responsible for such an effect is named breakdown field or breakdown strength ($E_{\text{break}}$). For most polymers, $E_{\text{break}}$ is in the range $10^6$–$10^8$ V/m. Up to now, it is still difficult to make a reliable prediction of $E_{\text{break}}$ according to the present physical models. In fact, there are several possible causes and processes related to dielectric breakdown. However, it is generally accepted that mechanisms responsible for dielectric discharges have both thermal and intrinsic (bulk) origins. In the first case, both dielectric polarization and conduction losses determine a temperature increase of the material. Indeed, the power density dissipated into the dielectric medium, at the expense of the electric field, is proportional to $k''_{\text{eff}}(\omega)$:

$$W \propto \omega |\vec{E}|^2 k''_{\text{eff}}(\omega)$$  \hspace{1cm} (8)

Such a heating, in turn, enhances the conductivity in a self-amplified process with catastrophic consequences. In fact, the amount of heat that the material is not able to dissipate drives it to the breakdown. As a second possibility, breakdown may be related to an avalanche discharge process that begins with the promotion of few valence electrons to the conduction band. These electrons, being accelerated by the applied electric field, strike against other valence electrons, driving them to the conduction band by a kinetic energy transfer; as this process of charge carrier multiplication goes on, the current flow grows rapidly in the dielectric and the material can locally melt.
2.4. Dielectric strength of random polymer–matrix composites

High-$k$ polymer composites are often used to store electric energy. The maximum energy storage density ($w_{\text{max}}$: J m$^{-3}$) of a material can be acquired via the following equation:

$$w_{\text{max}} = \frac{1}{2}k_0k_1E_{\text{break}}^2$$  (9)

In order to possess the maximum energy storage density, we must endow the material should have both high dielectric permittivity and high breakdown field at the same time. Nevertheless, in most practical applications, the electric field employed is less than the breakdown field. It is well-known that one of the typical drawbacks of the random composite approach lies in a substantial decrease in the material dielectric strength $E_{\text{break}}$. Higher values of $k'_e$ typically correspond to lower values of $E_{\text{break}}$. This experimental evidence is confirmed by an abundant literature [43] and might be reasonably interpreted as mainly due to interfacial (Maxwell–Wagner) polarization phenomenon [41–43,85,86]. Although a general expression capable of reliably relating the dielectric strength to the dielectric permittivity of composites is currently not available, it is worth reporting at least a couple of simple models that can help predict results to a certain extent.

The first model deals with a very rough schematization: consider the polymer as a homogeneous material and a purely elastic body at low strains. Under such conditions and in the case of Maxwell-stress actuation, the nominal breakdown field of the material is given by the following expression:

$$E_{\text{break}} = \frac{V_{\text{break}}}{d_0} = e^{-1/2} \sqrt{\frac{Y}{2k_0k'_e}} \approx 0.6 \sqrt{\frac{Y}{2k_0k'_e}}$$  (10)

where $k'_e$ is the dielectric permittivity of the material, $Y$ its elastic modulus, $V_{\text{break}}$ the breakdown voltage of the sample and $d_0$ its thickness at rest. This relation suggests that by increasing the dielectric permittivity of the material, its dielectric strength is expected to decrease as $1/\sqrt{k'_e}$. Interestingly, such a trend is often found to provide a satisfying fit to experimental data [87].

A delicate model is offered by the local field theory of dielectric media [88]. Consider a dielectric material subjected to an applied electric field $E$. Although the space-averaged electric field can be uniform, the actual internal electric field can locally vary from point to point, depending on interactions of local fields generated by dipoles. Accordingly, the local electric field $E_{\text{local}}$ is defined as the field that actually acts on an individual polarizable unit (such as a molecule or an atom); it is also known as the Lorentz local field and is given by the following expression [88]:

$$E_{\text{local}} = \frac{k' + 2}{3}E$$  (11)

where $k'$ is the dielectric permittivity of the material surrounding the local polarizable unit (excluding the unit itself). Eq. (11) can be used to obtain an expression that relates the dielectric permittivity and the dielectric strength of the matrix ($k'_m, E_{\text{break},m}$) with those of the resulting composite ($k'_c, E_{\text{break},c}$). In fact, if it is assumed that the value of the local breakdown field of the matrix is the same when the matrix is in its pure and its composite form by equating the right-hand member of Eq. (11) evaluated for these two situations, the following expression can be obtained:

$$\frac{k'_m + 2}{3}E_{\text{break},m} = \frac{k'_c + 2}{3}E_{\text{break},c}$$  (12)

Eq. (12) can be further developed by using $k'_c$, one of the mixing rules described below, according to different models. It provides a useful tool to estimate the overall electrical behavior of the composite system.
2.5. Theoretical models for dielectric properties of polymer–matrix composites

In a high-$k$ PMC, fillers impart mainly dielectric properties while the matrix phase imparts mechanical properties. Properties of composite generally show different trends in electrical properties compared to pure constituent phases. Several mixing rules have been proposed to account for the effective permittivity of a system consisting of two immiscible phases or multiphase.

2.5.1. Maxwell–Garnett equation

A number of models have been proposed and used for predicting the effects of second phases on the dielectric properties of the composites. Among these models, those pertaining to continuous media filled with spherical particles are considered as a starting point for discussion. To start with mixing rules, consider an isotropic medium (matrix) of dielectric permittivity $k_m$ filled with spheroids of permittivity $k_f$. The volume fraction of filler particles is designated as $\phi_f$ and the resulting volume fraction of the matrix $\phi_m = 1 - \phi_f$. It is assumed that both the filler and matrix components have no dielectric loss in frequency regions of interest.

For any two-phase composite one can write the lower permittivity, which denotes a series model as shown in Fig. 4a,

$$k_{c,\text{min}} = \frac{k_m k_f}{k_m \phi_f + k_f \phi_m}$$  \hspace{1cm} (13a)

and the upper dielectric permittivity, which corresponds to a parallel model as shown in Fig. 4b,

$$k_{c,\text{max}} = k_m \phi_m + k_f \phi_f$$  \hspace{1cm} (13b)

This means that for a given physical system, the dielectric function, $k_c$, must lie between these bounds. Namely, the permittivity of a two-phase composite is between the $k_{c,\text{min}}$ and $k_{c,\text{max}}$ ($k_{c,\text{min}} \leq k_c \leq k_{c,\text{max}}$), which can be described by mixing models with series and parallel in consistent with practical composites as shown in Fig. 4c.

Beyond such rough limits, further steps in modeling the dielectric properties of binary mixtures have been accomplished in the framework of the so-called Wagner theoretical schemes [89,90]. By equating these two alternative expressions, the so-called Sillars [91] or Landzu–Lifshitz [92] rules can be obtained as follows:

$$k_c = k_m \left[ 1 + \frac{3 \phi_f (k_f - k_m)}{2k_m + k_f} \right]$$  \hspace{1cm} (14)

However, these rules hold only for low volume fractions of filler and are restricted by electrical conductivity values of filler and matrix. More accurate equation for predicting dielectric properties can be achieved by the following equation known as Maxwell–Garnett equation [93–96].

$$k_c = k_m \left[ 1 + \frac{3 \phi_f (k_f - k_m)}{(1 - \phi_f)(k_f - k_m) + 3k_m} \right]$$  \hspace{1cm} (15)

Fig. 4. Ideal connection ways of two-phase composites, (a) series model, (b) parallel model, and (c) a mixing model, pink lines stand for electrodes.
This equation considers the dielectric permittivity arising from spherical fillers dispersed in a medium. It should be noted that Maxwell–Garnett rule does not consider the resistivity of medium or filler particles and hence gives advantage over Landu–Lifshitz mixing rule, which is limited only to composites where fillers should have higher electrical resistivity than matrix.

In the literature, Maxwell–Garnett equation is expressed in many forms and is also referred to several other names such as Maxwell–Wagner [97] or Rayleigh [98] or Lorentz–Lorenz [99] or Kernner-Bottcher [83] equation. One of such Maxwell–Garnett equation forms is given below,

$$
\frac{k_c - k_m}{k_c + 2k_m} = \frac{k_f - k_m}{k_f + 2k_m}
$$

This equation is applicable only to spherical particles. However, when dispersed particles are not spherical in shape, it needs to be modified in order to take into account the geometry of dispersed particles. A common way to include the information about the geometry of dispersed particles is to introduce a depolarization factor, which is related to their deviation from sphericity. Thus, Maxwell–Garnett could be changed into this form to make it more general [90].

$$
k_c = k_m \left[ 1 + \frac{\phi_f (k_f - k_m)}{A(1 - \phi_f)(k_f - k_m) + k_m} \right] \quad \text{for } \phi_f < 0.1
$$

where the parameter $A$ is the depolarization. When $A = 1/3$ equation turns back to Eq. (16). The value of $A$ can be calculated or can be found in the literature [80].

2.5.2. Bruggeman self-consistent effective medium approximation

Bruggeman proposed an improvement of mixing rules as an extension of the Wagner scheme, in which the initially low volume fraction of the filler is gradually increased by infinitesimal additions. Exact solutions of the Wagner’s theory for very common cases can also be shown as Bruggeman equation when the samples are lamellae or disks and the spherical fillers are used.

$$
k_c = k_f \frac{3k_m + 2\phi_f (k_f - k_m)}{3k_f - \phi_f (k_f - k_m)}
$$

The Bruggeman integration method leads to a distinct mixing rule, which permits to assess the overall electrical response at much higher content of spherical filler. This is particularly attractive for a disordered system, where constituent particles may become very close to each other and even agglomerate, so that deviations from an ideally uniform and dilute system may be substantial even at low filler concentrations ($\phi_f > 0.1$). Thus the solution of a differential equation obtained from either Eqs. (15) or (16) leads to the final Bruggeman’s formula [100,98]:

$$
\frac{k_f - k_c}{k_c^{1/3}} = \frac{(1 - \phi_f)(k_f - k_m)}{k_m^{1/3}}
$$

This equation is expected to hold for $\phi_f$ values up to 0.5, with the constraint that the dispersed spheres do not form a percolative path throughout the medium.

2.5.3. Jaysundere-Smith equation

Maxwell–Garnett equation is valid only for lower concentration of filler as shown in Fig. 5a. Since the interaction between filler particles is relatively weak, it is often neglected in the course of theoretical prediction for dielectric properties due to a large distance between filler particles. At higher concentration of fillers, the interaction between fillers is becoming significant because the distance between fillers is extremely close, especial for nanosized fillers as shown in Fig. 5b. Moreover, electrical field arising from the neat induced distribution of dipole moment is no more negligible when calculating overall field locally experienced in the matrix. Based on this assumption, Jaysundere and Smith proposed a more realistic mixing rule. They calculated the electric field with a dielectric sphere embedded in a continuous dielectric medium by taking into account polarization of adjacent particles and arrived at the following equation [83]:

$$
\phi_f (k_f - k_m)
$$
Lichtenker's idea was based on the Wiener theory for bounds of effective dielectric function or effective conductivity of a composite [101]. According to Weiner's theory, the lower and upper bounds are represented in Eqs. (13a) and (13b). The upper bound for this effective dielectric function is reached in a system consisting of plane-parallel layers disposed along the electric field. The lower bound is reached in a similar system, but with the layers perpendicular to the field. Similar results were obtained using the method of cross-sections. Starting from Eqs. (13a) and (13b), Lichtenker assumed that the effective dielectric function of the considered composite satisfies the equation:

\[
\frac{k_c}{k_m \phi_m + k_f \phi_f} = \frac{3k_m}{2k_m + k_f} \left[ 1 + \frac{3k_m}{2k_m + k_f} \right] \left[ 1 + \frac{3k_m}{2k_m + k_f} \right]^{-1}
\]

where the parameter \( \alpha \) varies from \(-1\) to 1. Thus, the extreme values of this \( \alpha \) index correspond to the Wiener boundary values. The parameter \( \alpha \) may be considered as describing a transition from anisotropy at \( \alpha = -1 \) to isotropy at \( \alpha = 1 \). Each \( \alpha \) value describes a specific microgeometrical topology of a composite. One can therefore expect that the applicability of Eq. (21) is wider than that of the well-known Maxwell–Garnett and Bruggeman equations that, in general, have no free parameters related to the topology. For Bruggeman’s theory, the filling factor may be considered as a parameter describing the topology; in particular, it specifies the percolation threshold, as will be discussed in Section 2.6. Several examples of applications of Lichtenecker’s equation can be found, especially in Ref. [101]. At the same time, it is not very clear for what systems this Eq. (21) is valid, and what is the range of its universality.

Percolation model

To increase the dielectric permittivity of polymers, the inorganic fillers mentioned in Section 2.5.1–2.5.4 are electrical insulators. The dielectric permittivity of inorganic fillers, such as ceramics powders, BaTiO\(_3\), PbTiO\(_3\), Pb(Zr,Ti)O\(_3\) (PZT), and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)–PbTiO\(_3\) (PMN–PT) is high. However, the dielectric permittivity of their polymer–matrix composites is still not high enough, even at high concentration of fillers [28,102–107]. Perhaps weak interfacial interaction and pores in composites are responsible for the low dielectric permittivity of the composites with ceramic fillers at high content [28,108–111]. In addition, the flexibility of the polymer–matrix composites is poor if the concentration of fillers employed is high [102–111]. Therefore, one must seek a new way to improve the dielectric permittivity of composites. Most recently, based on percolation theory, the permittivity of polymer–matrix composites is improved significantly using conducting fillers [19,20,50,51,55–60,68,72–75].
Although conductive fillers can result in high dielectric loss, a need for high-$k$ materials has pushed researchers to test the effect of loading of these fillers in polymers. The use of conducting fillers is motivated by the fact that they not only increase conductivity but also induce Maxwell–Wagner polarization. As a result, the polarization leads to a high dielectric permittivity in conductive filler–polymer composites. In general, the electrical conductivity of conductive filler–polymer composites exhibits a non-linear increase in dielectric value when the concentration of fillers is above a percolation threshold. This phenomenon cannot be explained by classical mixing rules but by percolation theories. At low concentration of filler, conductive particles are separated from each other (see Fig. 6a and b) and the electrical properties of the composites are dominated by the matrix. With increasing filler concentration, local clusters of particles are formed, which is shown in Fig. 6c. At the percolation threshold, these clusters form a connected three-dimensional network through the component (see Fig. 6d), resulting in a jump in the electrical conductivity.

The microstructures shown in Fig. 6 are isotropic, which are formed by spheres or spheroids with random orientation. When the spheroid grains of the minor phase are oriented, the microstructures become anisotropic, as shown in Fig. 7. Furthermore, if conducting fillers have a high aspect (length/diameter) ratio, the anisotropic microstructure of composites can more easily be formed. In this case, the percolation threshold in the oriented direction can be very low and the composite can exhibit excellent flexibility.

In fact, when the concentration of conducting fillers is close to the percolation threshold, the composites often display a metal–insulator transition in electrical property. Namely, the percolation threshold represents the filler concentration at which conducting paths come into contact with each other throughout the medium. The percolation theory allows estimating $f_c$ with power laws describing the conductivity and dielectric permittivity of the composite near the metal–insulator transition by fitting the experimental $\sigma$ data for $f_{\text{filler}} > f_c$ and $f_{\text{filler}} < f_c$. They often abide the following relations [19,20,50,80]:

![Fig. 6. Schemes showing the formation of a percolation-like clusters structure with an increase in the concentration of conducting fillers in a composite. (a) randomly dispersed grain structure; (b) uniformly dispersed grain structure; (c) aggregated grain structure; (d) percolation-like clusters structure [80].](image)

![Fig. 7. Schematic microstructure of a two-phase composite with oriented minor-phase spheroids [80].](image)
For electrical conductivity,
\[ \sigma_c \propto (f_{\text{filler}} - f_c)^t \quad \text{for } f_{\text{filler}} > f_c \]  
\[ \sigma_c \propto (f_c - f_{\text{filler}})^q \quad \text{for } f_{\text{filler}} < f_c \]  

For dielectric permittivity,
\[ k'_c \propto (f_c - f_{\text{filler}})^q \quad \text{for } f_{\text{filler}} < f_c \]  

where \( f_c \) is the percolation threshold, \( t \) the critical exponent in the conducting region, \( q \) the critical exponent in the insulating region, and \( q \) dielectric critical exponent. Two-phase random media normally have a value of about 0.16 for the percolation threshold. The universal values of the critical exponents \( q \) and \( t \) are commonly 0.8–1 and 1.6–2, respectively. The universality of percolation theory also suggests that the dielectric permittivity should exhibit the same power-law dependence on the volume fraction as the conductivity below \( f_c \), i.e., \( q \approx 1 \). However, this is not always observed in practical continuum systems [112].

The percolation threshold also depends upon the size and shape of conducting fillers. Common conductive fillers are metallic or graphitic and are in different shapes (spherical, platelet-like or fibrous)

---

**Fig. 8.** Ten connectivity patterns for two-phase composites [80,114].
and sizes. However, the incorporation of CNT, because of their large aspect ratio, allows for a low percolation threshold, as illustrated in Fig. 7 [50–56,113]. In addition, the dielectric values in these percolative systems are very sensitive to the concentration of fillers. A slight change in concentration near the percolation threshold can bring about a drastic change in dielectric properties. Parallel increases of dielectric permittivity and loss are frequently observed.

2.6. Connection type of PMC

Properties of composite materials depend not only on the type of filler and that of the matrix, but also on how they are coupled. This coupling concept is called connectivity and was first introduced by Newnham [114]. Consider the connectivity of a two-phase system. If a phase is self-connected in three directions, its connectivity is termed as 3. If self-connected in two directions, its connectivity is termed as 2, and so on. A binary composite connectivity is defined by combination of terms \(m-n\). Here \(m\) represents the connectivity of the active phase (filler) while \(n\) represents the connectivity of the inactive one (matrix). In general, there are 10 different patterns for binary composites on the basis of connectivity: 0–0, 0–1, 0–2, 0–3, 1–1, 1–2, 1–3, 2–2, 2–3, and 3–3, which are illustrated in Fig. 8. Herein, the 0–0, 0–1, 0–2, and 0–3 connectivity patterns in Fig. 8 are the dispersed grain structures, in which the 0–0 pattern is equivalent to the dispersed grain structure in Fig. 6b, and the 0–1, 0–2, and 0–3 patterns correspond to the dispersed grain structure in Figs. 6a and 7a. The 1–2, 2–3, and 1–3 connectivity patterns in Fig. 8 correspond to the aggregated grain structure in Fig. 6c, in which the minor phase grains in the 1–3 pattern are aggregated in the form of single chain-like clusters, and those grains in the 1–2 and 2–3 patterns are aggregated in the form of close-packed clusters. Similarly to Fig. 7b, the 1–1 and 2–2 connectivity patterns are specific cases of aggregated grain structures, in which the grains are aggregated along a definite direction as laminated structures. The 3–3 connectivity pattern in Fig. 8 stands for the percolation-like cluster structure in Figs. 6d and 7c in which the two phases form interpenetrating three-dimensional networks (percolation cluster). In current works, the 0–3 [115–120] and 1–3 [121–133] connectivity patterns are often designed to fabricate filler/polymer matrix composites.

3. Processes for the fabrication of high-\(k\) PMC

Homogeneous dispersion of fillers into polymer matrices is crucial to the properties of PMC, especially in the field of functional applications. All the processes used normally aim at distributing and dispersing the fillers in the polymer matrices in a desired manner. There are mainly two types of dispersion processes: solid phase processes and liquid ones. The former often call up mechanical approaches. Usually they are very simple and straightforward and rely directly on mixing the filler with the aid of mechanical force and can be used widely in practical production due to their convenience, low cost and mass production. Mechanical mixing processes can be divided into categories: direct mixing and melt mixing. A big disadvantage of mechanical mixing processes lies in relatively poor dispersion and weak interfacial interaction between fillers and polymer matrices in comparison to chemical ones (also named as liquid phase processes), which often ensure better dispersion of fillers and stronger interfacial interaction.

3.1. Solid phase processes

3.1.1. Direct compounding

Direct mixing involves the mixture of filler and polymer without any pre-treatment. Such a process was attempted by Haggenmüller et al. [134]. They cut into small pieces a MWNT/PMMA composite sample in which the MWNT were visibly not well dispersed. They mixed those pieces and hot pressed the mixture to create a new sample. They repeated this cutting and mixing procedure 20 times and found that the MWNT dispersion quality was improved. Their comment about the quality was based on sections of the sample observed under an optical microscope [26]. Wong et al. [135] prepared graphite nanostructured composites by ball milling, which reduced particle sizes to smaller platelets.
Not other critical advantages were noted. A bimodal distribution of 100 and 400 nm particles was observed using a particle analyzer. The ultimate objective was to develop an alternative cost-effective nano-scale carbon material with properties comparable to those of carbon nanotube based composites. Azhdar et al. investigated the compaction of polymer powders and PMMA based nanocomposites by uniaxial high-velocity cold compaction (HVC), high-energy ball milling (HEBM) and a relaxation assisted process [136]. It was found that a longer mixing time yielded a higher degree of dispersion of the NiFe$_2$O$_4$ nanopowder on the PMMA particle surfaces. Kim et al. [137] fabricated Al$_2$O$_3$-based polyimide composite thick films for integrated substrates by using benefits of aerosol deposition method. The relative permittivity and loss tangent of 3 wt%-Al$_2$O$_3$ composite film was 7.6 and 0.008 at 1 MHz, respectively. By employing a direct mixing process, Dang et al. fabricated PVDF composites based on MWNT [51], CF [58], Ni [19], BaTiO$_3$ [40], (Ni–BaTiO$_3$) [20], (MWNT–BaTiO$_3$) [57], PANI [75], and LTNO [35–37], respectively. Those composites showed different dielectric properties, depending on the type of the filler. A big disadvantage of the direct mixing process lies in that it is not efficient at dispersing fillers at the nanoscale if fillers tend to agglomerate. A pre-treatment for fillers is usually necessary to achieve reasonable dispersion. However, in some cases pretreatment still does not yield commendable results.

3.1.2. Melt compounding

To mix CNT with highly viscous fluids, especially thermoplastic melts such as PE and PS, one could rely on high shear forces to break down CNT aggregates and to improve CNT dispersion. Twin screw extruders are the most popular equipment for dispersing and processing CNT based composites owing to their good dispersive and distributive mixing capability [138–141]. Mechanical stir or magnetic stir could also be used to disperse CNT in lower viscosity solutions, usually thermosters or thermoplastics containing solvents. Moniruzzaman et al. mixed SWNT in epoxy at 100 rpm for 1 h in a twin–screw batch mixer (MicroCompounderw, DACA Instruments) and claimed that a uniform dispersion was achieved [142]. However, Sandler et al. used a stir to mix MWNT in epoxy at 2000 rpm for 5 min and still found MWNT aggregates dispersed in the resin [143]. The discrepancy shows the fact that the high speed mechanical stir or magnetic stir cannot generate sufficiently high shear stress to break down CNT aggregates as an extruder does. Safadi et al. [144] found that ultrasonic agitation improved the CNT dispersion by decreasing the CNT aggregates in size and in some cases even separated the CNT. However, the usefulness of ultrasonic agitation is limited to low viscosity media, such as water, acetone and dimethylformamide (DMF). For example, Vaccarini et al. obtained uniform SWNT dispersion in epoxy by sonicating SWNT and polymer with CH$_2$Cl$_2$ and then evaporating CH$_2$Cl$_2$ [145]. The use of ultrasonic agitation alone usually does not lead to uniform CNT suspension. Usually solution sonication is an important step combined with other methods to disperse CNT in polymer melts and solutions. It should be noticed that extrusion and ultrasonic agitation, the two most frequently used processes for dispersion, may cause damage to CNT surface and may also lead to attrition in CNT length which may be partially responsible for deterioration of mechanical properties of CNT based polymer composites. However, the viscosity of polymer melts usually increases after addition of fillers, especially at high concentrations of fillers. In such cases, processing of polymer melts becomes more and more difficult.

3.2. Liquid phase processes

3.2.1. Liquid-phase assisted dispersion

Dang et al. [29] reported a liquid-phase assisted dispersion method by utilizing ethanol as a dispersion medium to prepare uniformly dispersed BaTiO$_3$/PVDF nanocomposites. When the BaTiO$_3$ nanoparticles and PVDF particles were dispersed in ethanol at the same time, the former were inclined to absorb on the surface of the PVDF particles to form a special structure. This is because an interstitial hydrogen ion may exist in the BaTiO$_3$ lattice when BaTiO$_3$ nanoparticles are synthesized from a water solution [146]. In fact, BaTiO$_3$ nanoparticles also lean towards mutual attraction to reduce the surface energy. The mixture of BaTiO$_3$ nanoparticles and PVDF particles in ethanol reaches optimum dispersion by virtue of these two simultaneous adsorption actions. The result showed that the mixture with a suitable BaTiO$_3$/PVDF volume fraction ratio promoted the absorption of nanosized BaTiO$_3$
nanoparticles on the surfaces of the PVDF particles. Therefore, homogenous BaTiO$_3$/PVDF nanocomposites could be prepared by the natural adsorption effects occurring between the BaTiO$_3$ and PVDF particles when the BaTiO$_3$/PVDF volume ratio in the composite is appropriate. This powerful principle could be applied to acquire inorganic filler/polymer nanocomposites.

3.2.2. Solution route

At high filler concentration, melt mixing is not necessarily the best choice for composite processing because of higher viscosity of the mixture. By contrast, high concentrations of fillers can be incorporated into polymer matrices by using solution processing. This process involves dispersion of both polymer and filler in a solvent. However, most systems require the use of large volumes of solvents to fully dissolve the polymer and disperse the filler. Since common solvents such as toluene, chloroform, THF, or DMF are of high toxicity, a number of aqueous systems have been explored. Solution-casting has been used to manufacture MWNT-containing PS [144,147,148], PHAE [149,150], PVA [151], UHMWPE [152], and PP [153] composite films with homogeneous nanotube dispersions. Similarly, SWNT-containing PP [154], PVA [155,156], and PVA/PVP [157] composite films have been prepared. In many cases, ultrasonication processes are used to aid nanotube dispersion in liquid media. Nevertheless, prolonged high-energy sonication has the potential to introduce defects to nanotubes [158]. Ultrasonic treatment may also stabilize the dispersion by grafting polymers onto the CNT surface through trapping of radicals generated as a result of chain scission [159]. In addition, surfactants [157,160], polymer-functionalized nanotubes [151,155], and other chemical treatments of the constituents [161] are often employed. DMF dissolves PVDF well. As a result, it is often used to prepare filler/PVDF composites with high dielectric permittivity. After the PVDF is dissolved in DMF, filler particles such as ceramic particles and MWNT are mixed with PVDF solution, respectively [44,50,52–55]. In short, solution processes can be very efficient at dispersing fillers in PVDF solution.

3.3. In situ polymerization processes

In situ polymerization processes for fabricating polymer composites are usually associated with better filler to matrix interactions leading to improved electrical and mechanical properties. A number of works have used such processes to prepare nanotube–polymer composites [162–167]. Popielraz and Chiang [166] fabricated BaTiO$_3$/TMPTA and CdO/TMPTA composites by photo polymerization of TMPTA monomer in the presence of BaTiO$_3$ and CdO, respectively. Polymer composites obtained by this process showed dielectric permittivity comparable with that of BaTiO$_3$. The CdO/TMPTA composites showed relatively high dielectric permittivity and low dielectric loss as compared to those of BaTiO$_3$/TMPTA composites. Cochet et al. [167] prepared PANI/MWNT composites by an in situ polymerization process in the presence of MWNT. Their results revealed site-selective interaction between the quinoid ring of the PANI and MWNT, thus opening the way to charge transfer processes, and improving the electrical properties of the PANI/MWNT composites. Xiao and Zhou deposited polypyrrole or PMeT on the surfaces of the MWNT by in situ polymerization. The Faraday effect of the conducting polymer enhances the performance of super-capacitors with MWNT deposited with the conducting polymer. Xiao and Zhou [168] prepared CNT/PMMA composites by in situ polymerization of MMA in the presence of CNT.

To acquire materials with high dielectric permittivity and good thermal stability, Dang et al. called upon in situ polymerization processes to prepare BaTiO$_3$/PI composites [43] and CCTO/PI composites [45] with high dielectric permittivity, high electrical breakdown strength and high thermal stability. In situ polymerization processes allow for homogenous dispersion of functional fillers and therefore ensure strong interfacial interaction between the fillers and the polymer. As a result, the composites display excellent electrical properties.

In summary, the preparation process is very important for polymer composites because it has a crucial effect on their dielectric properties. The type of process and its operation conditions should be defined based on the physical, chemical, rheological and thermal characteristics of the system.
4. Microstructure and interfaces of high-\(k\) PMC

Often composites compose of more than two kinds of constituents. Composition, microstructure and interface of the composites have a crucial effect on the ultimate properties of materials [169,170]. To acquire composite materials with desired properties, it is very important to properly design their composition, microstructure and interface.

4.1. Two-phase high-\(k\) PMC

The behavior and performance of polymer composites cannot be understood solely on the basis of the inherent properties of its principal components. The interphase that exists between the filler and polymer is essential part of the composite. It is unanimously acknowledged by the scientific community that improvement in electrical and mechanical properties of composites is possible by full understanding of the interfacial region of composites. In traditional composites, the interfacial region is defined as the volume in which the properties deviate from those of the bulk matrix or filler [171]. However, it is simpler, in the case of uniformly sized spherical particles, to consider a straightforward calculation [172] of the interparticle distance \(l\):

\[
l = d \left( \frac{\pi}{6\phi_p} \right)^{1/3} - 1
\]

where \(d\) is the diameter and \(\phi_p\) is the volume fraction of the particles. For example, a 15 vol% loading of 10 nm diameter particles leads to an interparticle distance of only 5 nm, which is close to the radius of gyration of a typical polymer molecule. This shows that in such a case, the polymer matrix can behave as if it all belonged to an ‘interphase. In addition, the strong influence of interfacial interactions during processing can alter the matrix microstructure which can significantly affect the mechanical behavior of the nanocomposite independently of direct load-bearing by the filler [173]. This is especially so when the polymer is semicrystalline. Therefore, the matrix microstructure must be critically assessed when evaluating the performance of polymer composites. An important first stage to determine the microstructure of composites is to study the interaction between compounds participating in composite formation. Interaction between filler and polymer matrix can be chemical or physical or both. It is assumed that initial interaction way between polymer and filler can be a decisive factor in determining overall dielectric properties of composites.

Ceramic particles such as BaTiO\(_3\) [29,34,146,174,175], PMN–PT [28], PZT [107], LTNO [35–37] and CCTO [45,117] are often chosen as fillers to obtain two-phase high permittivity polymer composites. The latter composites may display different microstructures and interfacial interactions because of differences in size and surface characteristics of ceramic particles. Dang et al. explained strong attraction between BaTiO\(_3\) and PVDF on the basis of the microstructure of BaTiO\(_3\)/PVDF composites [29]. BaTiO\(_3\) nanoparticles would be inclined to absorb on the surface of the PVDF particles to form a half-baked core–shell structure. Kobayashi et al. [174] further clarified the effect of polarity of the polymer matrix on the final microstructure of polymer composites. Xie et al. [175] highlighted the importance of interactions between BaTiO\(_3\) and polyimide. To improve the interaction between filler and polymer, appropriate surface modification on fillers is often employed [34]. For example, Dang et al. reported that treatment of BaTiO\(_3\) surface with a coupling agent significantly improved the dielectric permittivity. This was attributed to stronger bonding between BaTiO\(_3\) and PVDF. The amount of the coupling agent also had a remarkable effect on the microstructure and interaction, as shown in Fig. 9. BaTiO\(_3\)/polyimide composites with high permittivity and good thermal stability were also prepared by an in situ polymerization process [43].

To prepare polymer matrix composites with even higher dielectric permittivity, LTNO and CCTO, two high permittivity ceramic fillers are often used [35–37,45,117]. The high permittivity of ceramics mainly originates from an internal boundary layer capacitance (IBLC) structure as illustrated in Fig. 10a [176–179].

Dang et al. reported CCTO/Pi functional hybrid films with high dielectric permittivity prepared using the in situ polymerization [45]. A surface morphological image of the hybrid film with
40 vol% CCTO filler is shown in Fig. 10b. It can be seen that the CCTO grains are dispersed in the PI matrix without any agglomeration. As such, the CCTO is coated by the PI and uniformly dispersed in the hybrid film after imidization, as shown on the fractured cross-surface of the CCTO/PI hybrid film in Fig. 10c. Moreover, the distribution of CCTO filler did not depend on the thickness of the film, indicating that the in situ polymerization process is effective for preparing CCTO/PI hybrid films. Fig. 10d shows that the grain particles of CCTO are not destroyed during the fabrication of the hybrid films and that the boundary layer surrounding the grains which was of the IBLC structure can be clearly seen. The choice of the grain particles size of a few micrometers was based on a balance between mechanical and dielectric properties of the hybrid films. The CCTO was also dispersed into P(VDF–TrFE) 55/45 mol% copolymer to prepare ceramic/polymer composites [117]. Although the solution-cast CCTO/P(VDF–TrFE) composite sample exhibits more pores, the six-layer hot-press sample after thermal annealing yields a dense microstructure, which is advantageous to the final high permittivity. The interaction between the polymer matrix and filler also has an important effect on the dispersibility of the filler in the polymer matrix. The strong interaction between PI and BaTiO3 particles led to the dispersion of BaTiO3 particles at the nanometer scale. Similar results were obtained for (Bi0.5Na0.5)0.94-Ba0.06TiO3–P(VDF–TrFE) 70/30 composites with 0.1 and 0.3 ceramic volume fractions [180].

Change of the microstructure of two-phase polymer composites with highly conducting filler is often from the change of the formed percolation structure when the concentration of conducting filler is close to critical value. Therefore, the microstructure as well as the percolation structure of the two-phase polymer composites depends on several factors such as the size, the shape and the spatial distribution of the particles within the polymer matrix, and the adhesion and the interactions between the two phases. These in turn depend on the preparation process. The influence of these factors on the percolation threshold is summarized in Refs. [181–184]. Zois et al. [185] explained the percolative
behavior of several metal/polymer composites based on the above viewpoints. Xu et al. reported the CB-filled polymer composites [184,186,187] with a double-percolation microstructure, which can be formed in binary-polymer–matrix composites [188]. In this case, an extremely low percolation threshold can be observed. Xu et al. reported. As shown in Fig. 11, Xu explained a typical composite consisting of CB particles, HDPE and PVDF with the double-percolation microstructure [189].

Compared to spherical fillers, the percolation microstructure can be formed at quite low critical value for the CNTs/polymer composites because of their large aspect ratio and small dimensions. A critical obstacle in using CNTs filler is that it is difficult to disperse them well in most polymer matrices because of the presence of strong interaction among nanotubes. The latter mainly originates from physical attraction via van-der walls forces, hydrogen bonding and chemical bonding. A great effort has been put to find suitable processes to disperse nanotubes into polymer matrices. One of the more effective ways is to create interfacial bonding between nanotubes and polymer matrices. For this purpose, surfaces of nanotubes are modified with certain organic groups such as carboxylic, fluoro, amino [50,190]. In fact, this method is not only limited to nanotubes but can also be used for other types of fillers. This increase in interfacial bonding promotes the dispersion of nanotubes, which in turn improves dielectric properties. Several studies have shown improved dielectric properties of composite after surface treatment of fillers like CNTs [191]. Dang et al. reported on a very high dielectric permittivity (8000) in functionalized carbon nanotube/electroactive polymer nanocomposites [50]. The very high permittivity was from the Maxwell–Wagner–Sillars (MWS) effect at the percolation and was caused by a thin insulating layer of PVDF that was part of the functionalized MWNT. However, it is very difficult to gauge interfacial bonding because no standard methods are available.

Researchers have also used atomic force microscopy to measure the force required to separate an embedded nanotube from a polymer matrix, which can be used to estimate the interfacial bonding. They could also align the nanotubes using mechanical stretching [192,193], extrusion [139], magnetic
field [194], and electric field [195]. This alignment of nanotubes further lowers percolation thresholds of CNT/polymer composites [196]. Fig. 12 shows the alignment of CNTs in PE under influence of magnetic filed. Fig. 13 gives the orientation of MWNT in PVDF parallel and perpendicular to tensile direction. In fact, the properties of CNT reinforced composites depend on orientation of CNT in addition to dispersion, aspect ratio and interfacial bonding. Wang et al. reported on the enhancement of electrical properties of ferroelectric polymers by PANI nanofibers with controllable conductivities [74]. Unlike 0-demension fillers with sphere shape and 1-demension fillers with fiber or tube shape, a high dielectric permittivity and low percolation threshold in nanocomposites based on PVDF and 2-demension exfoliated graphite nanoplates was reported [49]. The exfoliated graphite nanoplates can effectively increase the dielectric permittivity at percolation structure.
4.2. Three-phase high-k PMC

Though the volume concentration of ceramic fillers is up to 50–60%, the dielectric permittivity of the two-phase polymer composites consisting of ceramic particles with high dielectric permittivity and polymers is often low due to the composition and structure limitation of this kind of composites [28–34]. If the concentration of ceramic fillers is further increased, pores will appear so that the dielectric permittivity and the breakdown field decrease [28]. If the fillers in the polymer composites have a high electrical conductivity, according to the percolation theory the dielectric permittivity of the polymer composites increases rapidly [19,21–25]. In many papers, the dielectric permittivity up to several hundreds or several thousands has been reported [19,21,49,50]. However, a crucial issue is that the dielectric loss is very high so that the high-k PMC cannot be used in many fields because a great deal of heat will be produced under electrical field, which may not be acceptable. In order to overcome this problem, it is suggested that the three-phase polymer matrix composites consisting of ceramic phase, electrical conductive phase and polymer phase may be a good choice to require the high-k and low-dielectric-loss materials [20,27,197,198].

Dang et al. [20] reported a three-phase high-k PMC material consisting of BaTiO3 and Ni as inorganic fillers and PVDF as polymer matrix. When the volume fraction of BaTiO3 is 0.40, the dielectric permittivity of the (Ni–BaTiO3)/PCDF composites increases from 40 to 800 with increasing volume fraction of Ni from 0 to 0.23 (herein the percolation threshold is close to 0.23) and the dielectric loss is less than 0.5 at percolation. Additionally, the dielectric permittivity of this kind of three-phase polymer composite displays remarkable frequency dependence. Similarly, Devaraju and Lee [27] fabricated a three-phase PI composite by dispersing a prescribed amount of BaTiO3 in PAA solution. That solution was added to silver nanoparticles and was homogenized by stirring BaTiO3–PI mixture with 0.3 volume fraction of BaTiO3. The dielectric permittivity of 500 and dielectric loss of 0.23 at 100 kHz were observed at percolation. Shen et al. [197] proposed a three-phase system consisting of PVDF, metallic and magnetic particle Ni and ferrite particles. Ni particles were incorporated in ferrite-filled polymer matrix. Ni particles preferentially existed in the gaps between large ferrite particles as shown in the schematic Fig. 14. In such a three-phase system, large ferrite particles not only acted as a magnetic phase, but also as a high volume fraction, discrete phase confining polymers and metallic particle into continuous double-percolating structure. The addition of the secondary filler can bring about different morphologies owing to the interaction with the primary filler. As mentioned above, the presence of large ferrite particles in ferrite–polymer matrix forces Ni particles to reside in between them gives rise to clusters-like structure of Ni with a large aspect ratio, which otherwise might not be possible in a two phase Ni–polymer composite. A better understanding of morphology of three-phase composites can only be achieved by studying the interaction of fillers in polymer matrices.

![Fig. 13. Morphologies of samples ||a|| perpendicular and ||b|| parallel to the tensile-strain direction in the MWNT/PVDF composite with 2.0 wt% MWNT [52].](image-url)
Inorganic conductive particles can be used to improve the dielectric permittivity of polymer composites. Organic conductive particles may even be a better choice because they might have better compatibility with polymer matrices, which is helpful for improving the dispersion of organic particles in the polymers. Patil et al. [198] explained the possible interaction of fillers and polymer matrix in the three-phase composites where the secondary filler was PANI, an organic and conducting polymer. This unique microstructure of three-phase composites resulted in unique dielectric properties. It is very clear from examples above that the difference in nature of fillers can result in exceptional microstructure, which in turn will yield exceptional dielectric properties of these composites. By exploiting the unique microstructure, the dielectric properties as well as mechanical properties of three-phase polymer composites can be tailored to meet prescribed needs, which otherwise may not be possible for two-phase polymer composites. Huang et al. [68,70] reported on a fully functionalized high-dielectric-constant nanophase polymer with high electromechanical response by employing the copper phthalocyanine oligomer (PolyCuPc) as high dielectric-permittivity filler, PANI as conductive phase and PU as polymer matrix to form three-phase polymer composites. For these multicomponent nanocomposites, the high dielectric permittivity of the PolyCuPc enhances the dielectric permittivity of the PU matrix, while the conductive PANI raises the dielectric permittivity of the composite via the percolation structure. This combined two-phase dielectric matrix serves as the high-dielectric-constant host, and a dielectric permittivity near 1000 is achieved at 20 Hz. It is also explained that the enhanced dielectric response in the PolyCuPc graft PU could be attributed to the much-reduced filler size, which enhances the exchange coupling (an interface effect) as theoretically predicted by Li [199,200]. It is known that the CuPc and PolyCuPc have strong tendency to form stacked assemblies due to their planar shape and aromatic nature [201]. Since the pendant oligomer grafts are located separately along the polymer backbone and especially in the hard segments of the PU, the size of the aggregates is restricted by the accessibility of adjacent oligomer molecules in the polymer network [202,203]. During the deformation of the polymers under external fields, immobilization of the nanophases and polymer backbones via chemical bonding greatly reduces the relative motion and further aggregation of the nanophases within the polymer matrix, which improves the material reliability and breakdown field.

According to percolation, spherical conductive particles can be dispersed into polymers to improve the dielectric permittivity. However, their volume concentration at percolation is often higher than 10% [19–25,72]. Such a high loading of conductive particles results in a decrease in flexibility of the polymer composites. This is because spherical shape conductive particles have a low aspect ratio, which is not helpful to form the percolation structure. Thus, conductive fillers with high aspect ratio, such as CNT and CF, should be used for three-phase polymer composites [54,57,59]. Results of Dang et al. [54] show when the MWNT with a diameter of 20–40 nm and a length of 1–2 μm (aspect ratio = 25–100) is used as the conductive phase dispersed in the BaTiO3/polymer mixtures, the three-phase (MWNT–BaTiO3)/PVDF nanocomposites display significant enhancement in dielectric
permittivity. Furthermore, when the volume fraction of MWNT is 0.01 and 0.02 respectively, the increase in dielectric permittivity of the three-phase (MWNT–BaTiO$_3$)/PVDF nanocomposites is different, depending on the volume fraction of nanosize BaTiO$_3$ particles. The differences in dielectric properties can be attributed to the detailed microstructure of the three-phase (MWNT–BaTiO$_3$)/PVDF nanocomposites due to the concentration variation of MWNT and BaTiO$_3$. Fig. 15 shows TEM images of the fractured two-phase and three-phase composites with a fixed $f_{\text{MWNT}} = 0.02$. In the absence of nanosize BaTiO$_3$, MWNTs trend to be poorly dispersed and a network of aggregated MWNT bundles is observed (Fig. 15a). Moreover, a more effective three-dimensional conductive network has been formed because of the additional connection of the isolated MWNT bundles (as indicated by arrows in Fig. 15b) when the volume fraction of BaTiO$_3$ is increased to 0.05.

In contrast, the image of nanocomposites with the 0.20 volume fraction of BaTiO$_3$ shows significant improvement in MWNT dispersion. MWNT particles (as pointed by arrows in Fig. 15c) are well separated by BaTiO$_3$ particles rich areas. The aggregated MWNT bundles mentioned above cannot be seen any more. Fig. 16 shows schematic images of the microstructure of the (MWNT–BaTiO$_3$)/PVDF nanocomposites with a fixed MWNT content ($f_{\text{MWNT}} = 0.02$) and different concentrations of BaTiO$_3$. The threads and solid circles represent the MWNT and BaTiO$_3$ particles, respectively, and the region in dash circles shows the interfaces and microcapacitor structure. From the microstructure evolution processes, a critical concentration of BaTiO$_3$ particles (0.05) is found. Below 0.05, additional conductive network of MWNT bundles are induced (see Fig. 16b). However, above that critical volume fraction the conductive networks are interrupted rapidly with increasing concentration of BaTiO$_3$ (see Fig. 16c).

Generally speaking, by controlling the microstructure and interface of two-phase and three-phase polymer composites, the dielectric properties of the composites can be tailored. The composition of the multi-phase polymer composites and preparation process are important parameters for that purpose.

5. Effect of fillers on dielectric properties of high-$k$ PMC

Many factors would have an influence on dielectric properties of the polymer composites. Among them are the concentration, size and shape of fillers [7,20,28,36,37,43,45,80,117,205,206,191,207–209].

---

**Fig. 15.** TEM images of the fractured (MWNT–BaTiO$_3$)/PVDF composites with the volume fraction of BaTiO$_3$ at (a) 0, (b) 0.05, and (c) 0.20 [204].

**Fig. 16.** Schematic images of the microstructure of the (MWNT–BaTiO$_3$)/PVDF composites with the volume fraction of BaTiO$_3$ at (a) 0, (b) 0.05, and (c) 0.20 [204].
5.1. Concentration effect of fillers on dielectric properties

5.1.1. Effect of ceramic fillers

The increase in dielectric permittivity of the polymer composites containing inorganic fillers with low conductivity, such as ceramics, is due to the relatively high permittivity of ceramics compared to polymers. In addition, an increase in the content of ceramic fillers in the composites increases the interfacial area between the ceramic phase and polymer phase. As a result, the influence of interfacial polarization on the dielectric permittivity and dielectric loss can be significant. Accordingly the relative permittivity increases with ceramic loading. Generally, the dielectric loss of almost all ceramic/polymer composites increases with increasing ceramic filler loading. There are some exceptions to this rule. Namely, at higher filler loading, the particles trend to agglomerate resulting in an increase in porosity and a decrease in densification of composites. An increase in porosity leads to a decrease in dielectric permittivity because the permittivity of air is low. Generally, theoretical predictions are valid for lower volume fraction of filler loading [205,206]. This is attributed to imperfect dispersion of ceramic particles in polymer matrices. Many theoretical models suggest that fillers in a material should be ideally separated, non-interactive and roughly spherical shape. However, in practice they are not in such case. Many composites of interest in practice deviate markedly from this ideal configuration. Recent studies show that the interphase regions of ceramic/polymer composites have a relative permittivity significantly different from that of the polymer or ceramic phases [191]. Hence the effective permittivity of the composites depends on the permittivity of each phase in the mixture, their volume fractions, shape, size, porosity, interphase polarizability and interphase volume fractions. As a result, the effective permittivity has a nonlinear nature and consideration of all these parameters make the calculations tedious. These could be the reason for the deviation of experimental values of relative permittivity from theoretical ones at higher filler loading. In ceramic/polymer composites high filler loadings are generally necessary to achieve high dielectric permittivity. However, high ceramic loadings dramatically decrease the adhesion of the composites, which will reduce their processability and reliability of embedded capacitors. Therefore there is an upper limit for the ceramic loading in ceramic/polymer composites [210]. Bai et al. [28] reported when the volume percent of the ceramic powder was up to 60%, the measured dielectric permittivity of the composite became much lower than that predicted from the following equation:

$$k = k_p \left[ 1 + \frac{nq(k_c - k_p)}{nk_p + (k_c - k_p)(1 + \alpha)} \right]$$

(25)

where $k$ is the dielectric permittivity of the composite, $k_p$ and $k_c$ are the dielectric permittivities of the polymer matrix and ceramic, respectively. $\alpha$ is the volume fraction of ceramic and $n$ is a parameter related to the geometry of ceramic particles [207]. According to different models, Dang et al. [20]
showed the permittivity differences between experimental data of the BaTiO₃/PVDF composites and calculated ones by employing Maxwell–Garrett and Bruggeman equations mentioned in Chapter 2 (see Fig. 17).

Due to the effects of pores, interface interactions between ceramic and polymer, and the dielectric permittivity of ceramic particles, the improvement in dielectric permittivity of the ceramic particle/polymer composites is not very significant, whatever the types of ceramic particles, polymers and/or preparation processes used. For example, Chahal et al. [7] reported a value of dielectric permittivity of 39 for the 55 vol% ceramic/polyacrylonitrile composite and and 22 for the 50% ceramic/polyboronene composite. Bhattacharya et al. [208] reported values of dielectric permittivity of 9 and 34 for two kinds of composites for filler loadings of 21% and 46%, respectively. Dang et al. [29] reported that the dielectric permittivity of the BaTiO₃/PVDF nanocomposites is about 40 and 30 at 10³ and 10⁷ Hz, respectively. This indicates strong frequency dependence of dielectric permittivity. To acquire high-k PMC with excellent thermal stability, Dang et al. [43] reported on a BaTiO₃/PI nanocomposite prepared by in situ polymerization process. The dielectric permittivity is only 18 when the volume concentration of BaTiO₃ is 40%. However, it shows weak frequency dependence in the in situ prepared BaTiO₃/PVDF nanocomposite as shown in Fig. 18. [211] showed a direct assembly of BaTiO₃ (50 nm)/PMMA nanocomposite films by using electrophoretic deposition in the acetone/isopropyl alcohol (1:1) mixture solution with PMMA and BaTiO₃. As shown in Fig. 19, the nanosize BaTiO₃ particles can be dispersed in the PMMA homogeneously. The maximum dielectric permittivity of the BaTiO₃/PMMA nanocomposites reaches about 30 at 100 Hz when the volume content of BaTiO₃ is 60%, while a low dielectric loss (0.1) as shown in Fig. 19c. These results prove although the dielectric permittivity of conventional ceramic particles is about several thousands, the dielectric permittivity of the polymer composites is still low due to the effect of interface structure of the composites.

In order to further improve the dielectric permittivity of the polymer composites for a given ceramic concentration, two main methods can be employed [43]. One is to design and optimize the fabrication process so as to minimize pores in polymer composites [43, 117]. Another one is to develop novel ceramic fillers with very high dielectric permittivity by doping the metal oxides to form a boundary-layer capacitor structure [36, 37, 45, 108, 117, 179]. Dang et al. [43] reported that the dielectric permittivity of BaTiO₃/PI nanocomposites can be improved by a degassing process during in situ polymerization, which may reduce the pores in the final composites. Arbatti et al. [117] reported hot-pressed solution-cast films repeatedly at 200 °C in order to improve the uniformity and reduce the pore. During the hot-press process, a multilayer stack of solution-cast films was packed in a “sandwich” figuration. That is, the top of a solution cast film faced the top of another solution-cast film in the stack, whereas the bottom of the cast film faced the bottom of another cast film. The number of the solution-cast films in the stack was two, four, and six, respectively. Based on this stack process, the

![Fig. 18.](image_url)

(a) Dependence of dielectric permittivity on the volume concentration of BaTiO₃ of the BaTiO₃/PI composite films obtained by in situ polymerization. (b) Frequency dependence of dielectric permittivity of the BaTiO₃/PI composite film with BaTiO₃ loading at 40 vol%. Thermal imidization conditions were: 100, 200, and 300 °C for 1 h, respectively [43].
dielectric permittivity of the CCTO/polymer composites can be increased with more layers hot-pressed together as shown in Fig. 20a. After further annealing of the composites, the dielectric permittivity significantly increases (Fig. 20b). The detailed change in dielectric properties of the CCTO/polymer composites is also in Table 2. Dang et al. [37] reported LTNO/PVDF composites with high dielectric permittivity of about 600 at 40 vol% LTNO loading. Compared to the undoped ceramic fillers at the same concentration, the increase in permittivity with the doped ones is surprisingly high. The main reasons are related to the very high dielectric effect and semiconducting characteristics of the LTNO [177]. Compared to the LTNO/PVDF composites, the CCTO/PI composite films containing 40 vol% CCTO prepared by in situ polymerization had a maximum value of dielectric permittivity of about 50 at 100 Hz, which was 16 times larger than that of PI matrix [45]. The magnitude of increase in dielectric permittivity of the CCTO/PI composites is less significant than that in the LTNO/PVDF composites, which is about 60 times that of the PVDF matrix. However, the magnitude of increase in permittivity of the CCTO/PI composites is higher than that in the BaTiO3/PI nanocomposites [43], which can be attributed to the IBLC microstructure of CCTO fillers as shown in Fig. 12.
Kuo et al. [108] also reported on a multi-doped (La, Mg and Sr) BaTiO3 ceramic particles filled epoxy resin composites. After doping, the dielectric permittivity of the multi-doped BaTiO3 ceramic reaches 25,000, which is 10-times that of a classical undoped BaTiO3 ceramic. As a result, compared to the common BaTiO3/polymer composites at same concentration of fillers, the dielectric permittivity of the multi-doped BaTiO3/epoxy composites is extremely high. In Fig. 21a, the dielectric permittivity of the multi-doped BaTiO3/epoxy composites is as high as 45 at 40 vol% loading. Additionally, after doping and heat treatment at 900–1400°C for 1 h, as shown in Fig. 21b, temperature dependence of dielectric permittivity of the multi-doped BaTiO3/epoxy composites is so weak that the materials might be used within a wide temperature range. It is obvious that the dielectric permittivity of the polymer composites can be improved markedly by chemical doping to ceramic fillers so that the IBLC structure can be formed, which is charge of the high dielectric permittivity of ceramic fillers.

5.1.2. Effect of electrical conducting fillers

The dielectric permittivity of current polymer composites is still low and cannot satisfy the need of microelectronic industry. Flexible polymer composites with dielectric permittivity larger than 100 can be used in embedded capacitors applied at low working electrical field. This is a challenging issue. Fortunately, as discussed in Chapter 5.2, conducting fillers can markedly increase dielectric permittivity of polymer composites by taking the advantage of their percolative behavior. Polymer–metal composites show an abrupt increase in the permittivity near the percolation threshold and have a narrow smearing region [19,20,50,51,55–60,68,72–75,212–214]. A small change in filler concentration near the percolation threshold can drastically alter the dielectric properties of the composites. This may make the dielectric properties of polymer unpredictable and may render their applications difficult. Dang et al. [23] reported on high dielectric permittivity Ag/PI composite films with excellent thermal stability prepared by an in situ polymerization process as shown in Fig. 22. The effective dielectric

<table>
<thead>
<tr>
<th>Hot-press composites</th>
<th>Dielectric constant/loss (100 Hz)</th>
<th>Dielectric constant/loss (1 kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Two layers</td>
<td>245/0.32</td>
<td>483/0.21</td>
</tr>
<tr>
<td>Four layers</td>
<td>392/0.60</td>
<td>859/0.31</td>
</tr>
<tr>
<td>Six layers</td>
<td>362/0.43</td>
<td>838/0.41</td>
</tr>
</tbody>
</table>

Fig. 21. (a) Relative dielectric constants of the ceramic/polymer composite thick films, measured at 25 °C and 100 kHz, as a function of the volume fraction of multi-doped ceramic particles. (b) Variation of relative dielectric constant of the 30 vol% ceramic/polymer composite thick films with test temperatures for multi-doped ceramic fillers heat treated at 900–1400 °C for 1 h followed by 4 h milling, measured at 100 kHz [108].

Kuo et al. [108] also reported on a multi-doped (La, Mg and Sr) BaTiO3 ceramic particles filled epoxy resin composites. After doping, the dielectric permittivity of the multi-doped BaTiO3 ceramic reaches 25,000, which is 10-times that of a classical undoped BaTiO3 ceramic. As a result, compared to the common BaTiO3/polymer composites at same concentration of fillers, the dielectric permittivity of the multi-doped BaTiO3/epoxy composites is extremely high. In Fig. 21a, the dielectric permittivity of the multi-doped BaTiO3/epoxy composites is as high as 45 at 40 vol% loading. Additionally, after doping and heat treatment at 900–1400 °C for 1 h, as shown in Fig. 21b, temperature dependence of dielectric permittivity of the multi-doped BaTiO3/epoxy composites is so weak that the materials might be used within a wide temperature range. It is obvious that the dielectric permittivity of the polymer composites can be improved markedly by chemical doping to ceramic fillers so that the IBLC structure can be formed, which is charge of the high dielectric permittivity of ceramic fillers.

5.1.2. Effect of electrical conducting fillers

The dielectric permittivity of current polymer composites is still low and cannot satisfy the need of microelectronic industry. Flexible polymer composites with dielectric permittivity larger than 100 can be used in embedded capacitors applied at low working electrical field. This is a challenging issue. Fortunately, as discussed in Chapter 5.2, conducting fillers can markedly increase dielectric permittivity of polymer composites by taking the advantage of their percolative behavior. Polymer–metal composites show an abrupt increase in the permittivity near the percolation threshold and have a narrow smearing region [19,20,50,51,55–60,68,72–75,212–214]. A small change in filler concentration near the percolation threshold can drastically alter the dielectric properties of the composites. This may make the dielectric properties of polymer unpredictable and may render their applications difficult. Dang et al. [23] reported on high dielectric permittivity Ag/PI composite films with excellent thermal stability prepared by an in situ polymerization process as shown in Fig. 22. The effective dielectric

<table>
<thead>
<tr>
<th>Hot-press composites</th>
<th>Dielectric constant/loss (100 Hz)</th>
<th>Dielectric constant/loss (1 kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Two layers</td>
<td>245/0.32</td>
<td>483/0.21</td>
</tr>
<tr>
<td>Four layers</td>
<td>392/0.60</td>
<td>859/0.31</td>
</tr>
<tr>
<td>Six layers</td>
<td>362/0.43</td>
<td>838/0.41</td>
</tr>
</tbody>
</table>

Fig. 21. (a) Relative dielectric constants of the ceramic/polymer composite thick films, measured at 25 °C and 100 kHz, as a function of the volume fraction of multi-doped ceramic particles. (b) Variation of relative dielectric constant of the 30 vol% ceramic/polymer composite thick films with test temperatures for multi-doped ceramic fillers heat treated at 900–1400 °C for 1 h followed by 4 h milling, measured at 100 kHz [108].
permittivity of the film with 12.5 vol% of Ag fillers achieved 400 at $10^3$ Hz. The relative tolerance of the dielectric permittivity of the film with 12.0 vol% of Ag fillers in a wide temperature range was less than 4.0%, which would satisfy the need in practical applications. Qi et al. [21] also reported on an Ag/epoxy nanocomposite with 22 vol% of Ag having a high dielectric permittivity of 308 and a relatively low dielectric loss of 0.05 at $10^3$ Hz as shown in Fig. 23. In this composite material, 40 nm Ag particles coated with a thin layer of mercaptosuccinic acid were randomly distributed in the polymer matrix.

Because of the low performance of inorganic fillers such as ceramic particles and metal particles for flexible polymer composites, very recently organic fillers with high electrical conductivity have been used to improve the dielectric properties of polymer composites [72,74–76]. Huang et al. [72] recently reported on a high-dielectric-constant all-polymer percolative composite consisting of surface coated PANI (c-PANI) particles (less than 1 μm) and P(VDF–TrFE–CTFE) terpolymer with relatively high room-temperature dielectric permittivity (>50). In this c-PANI/P(VDF–TrFE–CTFE) composite system, upon changing the concentration of c-PANI, the dielectric permittivity close to 1000 at $10^3$ Hz is observed when the volume fraction of c-PANI is 23%, which is about 50 times higher than that of the terpolymer. Dang et al. [76] reported on a remarkable increase of dielectric permittivity in the PANI/PVDF nanohybrid films at low volume fraction of PANI (4.2%) shown in Fig. 24, owing to the use of PANI with about 50 nm average diameter and special preparation process.

![Fig. 22.](image)

(a) Dielectric permittivity (left side) and conductivity (right side) of the Ag/PI composite films as a function of the volume fraction of Ag at $10^3$ Hz and room temperature. (b) Temperature dependence of permittivity of the Ag/PI composite film (12 vol%) at different frequencies [23].

![Fig. 23.](image)

(a) Evolution of dielectric permittivity in the Ag/epoxy composites as a function of silver volume fraction at room temperature. (b) Dielectric permittivity of the Ag/epoxy composites with different concentrations of silver as a function of temperature at $10^3$ Hz [21].
Compared to the use of ceramic fillers, the use of conductive fillers can improve the dielectric permittivity of the polymer composites to a greater extent and at low loading of conductive fillers. A low loading of filler allows retaining the flexibility of polymers as much as possible.

5.2. Size effect of fillers on dielectric properties of PMC

5.2.1. Change in physical properties of fillers with size reduction

Size is an important property of fillers. Understanding the effects of the size and size distribution of fillers help understand the dielectric properties of the filler/polymer composites. Since the physical and chemical properties of fillers depend very much on size, especially when the sizes are smaller than 100 nm. In this size range, the bulk properties of the materials gradually disappear and approach molecular behavior when the sizes approach about 1 nm. The band gap opening increases with decreasing particle size. Some measured and calculated data for the effect of particle size on the band gap of nanoparticles is displayed [215]. In addition, the dielectric permittivity also depends on particle size. If the size of particles dispersed in the polymer matrix is in the order of nanometer, the dielectric permittivity of the particles is dependent on size. Many expressions for obtaining the size-dependent dielectric permittivity have been proposed. For example, the size-dependent dielectric permittivity on a nanocrystal is approximated in the following equation [171]:

\[
\frac{1}{k_{nc}(a)} = \frac{1}{k_{nc}^{\infty}(a)} - \beta(a) \left[ \frac{1}{k_{nc}(a)} - \frac{1}{k_{nc}^{\infty}(a) + 3.5} \right]
\]

(26)

And the electronic contribution to the total polarizability is shown in the following equation:

\[
k_{nc}^{\infty}(a) = 1 + \frac{k_{\text{bulk}}^{\infty} - 1}{1 + (3.75/a)^{1/2}}
\]

(27)

where \(a\) is in Angstrom units, and \(\beta(a)\) indicates how much the ions participate in the screening.

Small size of fillers leads to an exceptionally large interfacial area in the composites. Fig. 25a shows the surface area per unit volume as a function of particle size for spherical particles that are ideally dispersed. Fig. 25b shows interparticle spacing as a function of particle size for an ideally dispersed nanoparticle composite: at low volume fractions the entire matrix is essentially part of the interfacial
region. For example, for 15 nm particles at 10 vol% loading of filler, the interparticle spacing is only 10 nm. Even if the interfacial region is only a few nanometers, very quickly the entire polymer matrix has a different behavior than the bulk. Therefore, by controlling the degree of interaction between the polymer and the nanofiller, the properties of the entire composites can be controlled. To achieve novel properties of polymer composites, processing methods that lead to controlled particle size distribution, dispersion, and interfacial interactions are critical. Processing technologies for nanocomposites are different from those for composites with micrometer-scale fillers, and new developments in nanocomposite processing have contributed to their recent success.

5.2.2. Dependence of dielectric properties of PMC on size of fillers

Fillers with different particle sizes are found to affect dielectric properties of polymer composites. Kobayashi et al. [172] prepared BaTiO3/PVDF composites with different BaTiO3 particle sizes in nanometer scale. The dielectric permittivity and dissipation factor of composites increased with increasing crystal size of BaTiO3 particle as shown in Fig. 26. Similar results were also obtained [216]. However, Dang et al. used BaTiO3 particles having different sizes in micrometer range and obtained different results [40]. These BaTiO3/PVDF composites with different sizes and concentrations of BaTiO3 particles were fabricated via a simple physical mixing and subsequently hot-press processing. In order to study the effect of particle size on the dielectric properties of the SrTiO3/PEEK composite system, a comparative study has been performed with nanosize and microsize SrTiO3 fillers with 27 wt% loading [217]. Table 3 compares the permittivity, loss tangent and temperature coefficient of permittivity of 27 wt% micron- and nano-SrTiO3 filled PEEK composites. Interestingly, the permittivity, loss tangent as well as the temperature coefficient of permittivity ($T_{kr}$) of the nanosized SrTiO3 filled PEEK composites are higher than those of the microsized SrTiO3 filled composites. Because of the high surface area, polarizability also increases. This is because more charge can be accumulated on the grain boundary of the nanosized powder. Hence, the increase in permittivity of the PEEK nanocomposite can be attributed to the high polarizability of the nanosized SrTiO3 filler. However, the increase in loss tangent of the PEEK/
nano SrTiO3 filler at 27 wt% loading is believed to be caused by the lattice strain associated with the reduction in particle size.

Presently, the dielectric properties of materials are often measured in a relatively high frequency range. Therefore, it is difficult to reveal their dielectric properties of polymer composites with fillers of different sizes at ultra-low frequencies. By employing a broad frequency high resolution dielectric analyzer (Novocontrol), Dang et al. [41] found highly enhanced low-frequency dielectric permittivity in BaTiO3/PVDF nanocomposites with 100, 200, 300, 400 and 500 nm BaTiO3 particles, respectively. Fig. 27 shows the frequency dependence of the dielectric properties of the BaTiO3/PVDF nanocomposites with fillers of different sizes at 60 vol% loading. It is clear that the composite with 100 nm particles exhibits the maximal permittivity from $10^{-1}$ Hz to $10^{2}$ Hz and the appearance of the loss tangent peak is at about $10^{2}$ Hz. Fig. 28 shows the effect of the filler size on the dielectric permittivity in the BaTiO3/PVDF nanocomposites.

Table 3

<table>
<thead>
<tr>
<th>Powder characteristics</th>
<th>$k$ at 1 MHz</th>
<th>$\tan \delta$ at 1 MHz</th>
<th>$T_{kr}$ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micronsize powder</td>
<td>5.27</td>
<td>0.0037</td>
<td>12</td>
</tr>
<tr>
<td>Nanosize powder</td>
<td>5.9</td>
<td>0.0278</td>
<td>444</td>
</tr>
</tbody>
</table>

nano SrTiO3 filler at 27 wt% loading is believed to be caused by the lattice strain associated with the reduction in particle size.

Presently, the dielectric properties of materials are often measured in a relatively high frequency range. Therefore, it is difficult to reveal their dielectric properties of polymer composites with fillers of different sizes at ultra-low frequencies. By employing a broad frequency high resolution dielectric analyzer (Novocontrol), Dang et al. [41] found highly enhanced low-frequency dielectric permittivity in BaTiO3/PVDF nanocomposites with 100, 200, 300, 400 and 500 nm BaTiO3 particles, respectively. Fig. 27 shows the frequency dependence of the dielectric properties of the BaTiO3/PVDF nanocomposites with fillers of different sizes at 60 vol% loading. It is clear that the composite with 100 nm particles exhibits the maximal permittivity from $10^{-1}$ Hz to $10^{2}$ Hz and the appearance of the loss tangent peak is at about $10^{2}$ Hz. Fig. 28 shows the effect of the filler size on the dielectric permittivity in the BaTiO3/PVDF nanocomposites.

Fig. 26. (a) Dielectric constant and dissipation factor of the BaTiO3/PVDF composite films measured at $10^4$ Hz as a function of BaTiO3 crystal size. BaTiO3 volume fraction: 30%, spin speed: 3000 rpm and drying temperature: 150 °C [172].

Fig. 27. Frequency dependences of (a) dielectric permittivity and (b) loss tangent of all BaTiO3/PVDF composites at room temperature. The inset in (a) is the dependence of dielectric permittivity on frequency ranging from $10^2$ to $10^7$ Hz [41].
PVDF nanocomposites. At low frequency, the dielectric permittivity decreases with increasing BaTiO₃ particle size. The result could be explained by a marked increase in interfacial area and dipole polarizations at low frequency.

It can be seen that in the above mentioned examples, the dielectric permittivity of composites is clearly dependent upon the size of fillers. Nevertheless, trend of the dependence is not always the same. In some cases dielectric permittivity increased with increasing filler size and in some others cases it follows an opposite trend. One of the reasons is that change in dielectric properties with size in micrometer scale is not necessarily the same as that in nanometer scale. Another reason is the effect of the matrix on the effective crystal size of particles inside the composite and the interactions between the particles and the polymer matrix. The concept of effective filler is very important. Most filler size measurements are made on the powder samples before use. However, composite properties depend on the filler morphology in the final composite which may be significantly different from the initial filler morphology because of the effects of compounding and molding. The extent to which fillers are modified depends upon inherent filler properties and processing.

Percolation probability is closely related to the size of the conducting fillers in the composites. In classic models [218] for bulk samples, the insulating matrix is considered to be infinitely large in three dimensions compared with the size of filler. Therefore the influence of the filler size should be negligible. However for practical application such as embedded capacitor, a film with a thickness in micrometer is required to increase packaging density. In this case, classic models may not be valid, especially when the filler size is comparable to film thickness. Thus for dielectric composites used in embedded capacitor applications, the size of filler should be in nanometer to achieve high packaging density. For conducting fillers, the effect of size and size distribution of fillers on dielectric properties has been studied [22]. For example, Lu et al. [22] reported that the size, size distribution and loading level of in situ formed Ag nanoparticles in the Ag/CB/epoxy composites were found to have significant influences on the dielectric properties of the nanocomposite system. Fig. 29 indicates that the dielectric permittivity and dielectric loss of Ag/CB/epoxy composites with Ag nanoparticles of different sizes and size distributions varied considerably. A plausible explanation on those results may be that the interfacial loss due to the newly induced interface is higher than the suppressed conduction loss by incorporation of metal nanoparticles. Therefore, the overall dissipation factor is still increased for samples with a higher loading. Table 4 summarizes some examples of the effect of filler size on dielectric properties in various composition composites.

5.2.3. Effect of micro–nanosize cofillers on dielectric properties of PMC

To further improve the dielectric permittivity, the dense packing-density of ceramic/polymer composites is important. Particles with different sizes were filled into the polymer at same time so that the dielectric permittivity of the cofilled composites is higher than that of single-size filled composites at
the same concentration of fillers [33,40,42,219]. Cho et al. [33] reported the maximum dielectric constant of embedded capacitor films using 0.916 μm BaTiO3 particle (P1) was only about 57. After finer particles (0.06 μm in diameter (P2)) were added to 60 vol% P1, the powder packing density was further

Table 4

<table>
<thead>
<tr>
<th>Materials</th>
<th>$k$</th>
<th>tan$δ$</th>
<th>Filler size</th>
<th>Filler loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO3/epoxy</td>
<td>40</td>
<td>0.035 (1 Hz)</td>
<td>100–200 nm</td>
<td>60 vol%</td>
</tr>
<tr>
<td>Pb(Mg1/3Nb2/3)O3–Pb TiO3/P(VDF–TrFE)</td>
<td>~200 (10 kHz)</td>
<td>0.1 (10 kHz)</td>
<td>0.5 μm</td>
<td>50 vol%</td>
</tr>
<tr>
<td>Bimodal BaTiO3/epoxy</td>
<td>90</td>
<td>0.03 (100 kHz)</td>
<td>916 nm + 60</td>
<td>75 vol%</td>
</tr>
<tr>
<td>PMN–PT + BaTiO3/high-k epoxy</td>
<td>~150 (10 kHz)</td>
<td>N/A</td>
<td>900 nm/50 nm</td>
<td>85 vol%</td>
</tr>
<tr>
<td>BaTiO3/P(VDF–HFP)</td>
<td>37</td>
<td>&lt;0.07 (1 MHz)</td>
<td>~30 nm</td>
<td>50 vol%</td>
</tr>
<tr>
<td>CB/epoxy</td>
<td>13,000 (10 kHz)</td>
<td>3.5 (10 kHz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag/CB/epoxy</td>
<td>2260 (10 kHz)</td>
<td>0.45 (10 kHz)</td>
<td>Ag: 13 nm</td>
<td>Ag: 3.7 wt% CB: 20 wt%</td>
</tr>
<tr>
<td>Al/Ag–epoxy</td>
<td>160  (10 kHz)</td>
<td>0.045 (10 kHz)</td>
<td>Ag: &lt;20 nm</td>
<td>Al: 80 wt%</td>
</tr>
<tr>
<td>Ag/epoxy</td>
<td>~300 (1 kHz)</td>
<td>0.05 (1 kHz)</td>
<td>40 nm</td>
<td>22 vol%</td>
</tr>
<tr>
<td>Ag@C/epoxy</td>
<td>&gt;300 (1 kHz)</td>
<td>&lt;0.05 (1 kHz)</td>
<td>80–90 nm core</td>
<td>25–30 vol%</td>
</tr>
</tbody>
</table>

Fig. 29. Effect of size of Ag nanoparticles on (a1) dielectric permittivity and (a2) dissipation loss of 4.2Ag/19.6CB/epoxy composites (solid curves) and (b1) dielectric permittivity and (b2) dissipation loss of 6.2Ag/14.6CB/epoxy composites (dashed curves) [22].

Table 4

<table>
<thead>
<tr>
<th>Materials</th>
<th>$k$</th>
<th>tan$δ$</th>
<th>Filler size</th>
<th>Filler loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO3/epoxy</td>
<td>40</td>
<td>0.035 (1 Hz)</td>
<td>100–200 nm</td>
<td>60 vol%</td>
</tr>
<tr>
<td>Pb(Mg1/3Nb2/3)O3–Pb TiO3/P(VDF–TrFE)</td>
<td>~200 (10 kHz)</td>
<td>0.1 (10 kHz)</td>
<td>0.5 μm</td>
<td>50 vol%</td>
</tr>
<tr>
<td>Bimodal BaTiO3/epoxy</td>
<td>90</td>
<td>0.03 (100 kHz)</td>
<td>916 nm + 60</td>
<td>75 vol%</td>
</tr>
<tr>
<td>PMN–PT + BaTiO3/high-k epoxy</td>
<td>~150 (10 kHz)</td>
<td>N/A</td>
<td>900 nm/50 nm</td>
<td>85 vol%</td>
</tr>
<tr>
<td>BaTiO3/P(VDF–HFP)</td>
<td>37</td>
<td>&lt;0.07 (1 MHz)</td>
<td>~30 nm</td>
<td>50 vol%</td>
</tr>
<tr>
<td>CB/epoxy</td>
<td>13,000 (10 kHz)</td>
<td>3.5 (10 kHz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag/CB/epoxy</td>
<td>2260 (10 kHz)</td>
<td>0.45 (10 kHz)</td>
<td>Ag: 13 nm</td>
<td>Ag: 3.7 wt% CB: 20 wt%</td>
</tr>
<tr>
<td>Al/Ag–epoxy</td>
<td>160  (10 kHz)</td>
<td>0.045 (10 kHz)</td>
<td>Ag: &lt;20 nm</td>
<td>Al: 80 wt%</td>
</tr>
<tr>
<td>Ag/epoxy</td>
<td>~300 (1 kHz)</td>
<td>0.05 (1 kHz)</td>
<td>40 nm</td>
<td>22 vol%</td>
</tr>
<tr>
<td>Ag@C/epoxy</td>
<td>&gt;300 (1 kHz)</td>
<td>&lt;0.05 (1 kHz)</td>
<td>80–90 nm core</td>
<td>25–30 vol%</td>
</tr>
</tbody>
</table>

Fig. 30. (a) Dielectric constant changes with BaTiO3 powder loading. (b) Cross section image of ECFs containing bimodal BaTiO3 powders at 70 vol% (P1 60 vol% + P2 10 vol%) [33].
improved because the finer particles could fill interstitial sites of coarser particles [220]. As a result, at 75 vol% bimodal powder loading, a dielectric constant of 90 was achieved as shown in Fig. 30a. Further powder addition over 75 vol% at bimodal condition decreased dielectric constants of embedded capacitor films. Fig. 30b shows a cross section image of the embedded capacitor film containing 70 vol% (60 vol% P1 + 10 vol% P2) bimodal BaTiO3 powders. Dang et al. [42] reported on theoretical prediction and experimental study of dielectric properties in PVDF-matrix composites with micro–nanosize Ba-TiO3 filler. The dielectric permittivity of composites with nanosize BaTiO3 is close to the predicted values at high concentrations of fillers. The enhanced dielectric permittivity as shown in Fig. 31 mainly originates from a noticeably increasing phase interfaces in the composites due to micro–nanosize Ba-TiO3 cofillers, which brings about a strong interfacial polarization effect at low frequencies. Compared to the morphology of the single model BaTiO3/PVDF composite shown in Fig. 32, the stacking density of the double model composite is higher than that of the single model composite because the nanosize BaTiO3 occupies the spaces among the large BaTiO3 particles. The detailed change in dielectric properties of the BaTiO3/PVDF composites with different volume ratios of BaTiO3 fillers is also studied with fillers of different sizes (1000, 700 and 100 nm) [219].

5.3. Shape effect of fillers on dielectric properties

5.3.1. Shape of fillers and filler–polymer connectivity

A general classification of fillers on the base of particle shape has been presented [221]. This classification is somewhat arbitrary and is based on the primary properties of particle size and surface area, both of which being directly measurable and serve as systemizing filler functions. Shape of filler can be divided on the basis of whether they are one, two or three dimensional. Along with size of filler, shape of filler is decisive in determining dielectric properties of final composites. Filler with different shapes has different surface areas resulting in different interfacial areas in the composites, which can lead to different interfacial polarization and hence different dielectric properties. Moreover, different shapes of fillers can lead to different types of connectivity in composites. A schematic of different types of connectivities in high-κ PMC based on filler shape are presented in Fig. 33. In general, the 0–3 connectivity composites could be formed when the fillers are sphere particles and 1–3 connectivity composites when the fillers are fiber or tube by means of blending technique.

Different types of fillers including spherical, cubic and fiber and flakes have been used in high-κ PMC. For both of percolative and non-percolative composite systems, spherical fillers are amongst the most used fillers. Typical examples are ceramic and metal particles. For non-percolative systems containing spherical particles, common mixing rules like those mentioned in Chapter 2 can be used to explain the dielectric behavior of composites. However, when the dispersed particles are not spherical in shape, the mixing formulas must be revised, in order to take into account their geometry. A typical case is particles with a spheroidal or cylindrical geometry, characterized by the ratio of their axes.
common way to include the information about such kinds of geometries of fillers is to properly introduce a depolarization factor, which contains the information about the shape of particles in terms of their deviation from sphericity. Thus, for example, the widely used Maxwell–Garnett equation is modified into the other forms mentioned in Chapter 2.

5.3.2. Effect of 1-dimensional fiber-shape fillers on dielectric properties

For percolative systems, the more the shape of filler deviates from spherical particles, the lower is the percolation threshold. In other words, the high aspect ratio of fillers would induce a low percolation threshold. The most common high aspect ratio fillers incorporated in composites are CNT and CNF. CNT has typical diameter in the range of about 1–50 nm and length of many microns (even centimeters in some cases). They can consist of one or more concentric graphitic cylinders. In contrast, commercial (PAN and pitch) CF are typically in the 7–20 μm diameter range, while vapor-grown carbon fibers (VGCFs) have intermediate diameters ranging from a few hundred nanometers up to around a millimeter. Crucially, conventional carbon fibers do not have the same potential for structural perfection that can be observed in CNTs. Indeed, there is a general question as to whether the smallest CNTs should be regarded as very small fibers or heavy molecules, since the diameters of the smallest nanotubes are similar to those of common polymer molecules. This ambiguity is characteristic of nanomaterials, and it is not yet clear to what extent conventional fiber-composite understanding can be extended to CNT-composites. SWNTs are usually obtained in the form of so-called ropes or bundles, containing between 20 and 100 individual tubes packed in a hexagonal array [222–225]. Rope formation is energetically favorable due to the Van der Waals attractions or other interactions between isolated nanotubes [226]. MWNTs provide an alternative route to stabilization. They consist of two or more coaxial cylinders, each rolled out of single sheets, separated by the interlayer spacing in graphite. The outer diameter of such MWNTs can vary between 2 and a somewhat arbitrary upper limit of about 50 nm; the inner hollow core is often (though not necessarily) quite large with a diameter commonly about half of that of the whole tube.

As mentioned in Section 5.1, when spherical conducting fillers are used to improve the dielectric properties such as dielectric permittivity and conductivity, the percolation threshold is often high. This is a big disadvantage for flexibility of polymer composites. Therefore, conducting fillers with high aspect ratio are often used in order to have a low percolation threshold [49–56,74,121,123]. The morphology of CNT has a remarkable effect on the dielectric properties of nanotube containing composites. For example, entangled nanotubes usually need higher concentrations to achieve the percolation threshold while lower percolation threshold can be achieved with aligned nanotubes. Higher aspect ratio of nanotube is an obvious advantage for their use in high-k composite. However, in some cases higher concentrations tend to give rise to the entanglement of nanotubes destroying their effectiveness. Yao et al. [55] studied the effect of aspect ratio of MWNT on the percolation threshold as shown in Fig. 34. An increase in dielectric permittivity with increasing aspect ratio (AR) of
MWNT was observed in the composites. Meanwhile, the change in percolation threshold was complex and at the first glance surprising. The percolation threshold first increased with increasing AR, reached a maximum at a certain AR and then decreased with further increasing AR. Entanglement of the nanotubes would explain the results. An increase in the entanglement of nanotubes results in an increase in the percolation threshold. It is likely that the entanglement reduced the effective aspect ratio of the nanotubes. As MWNT become more flexible with increasing AR, they may have strong tendency to form interlocked inherent structures, like group of threads, and would not exhibit rod like rigidity anymore. In spite of nanotube entanglement at higher concentration, MWNT provide enough conductive paths to eclipse the effect of entanglement and would results in lower percolation threshold in practice. The same results were also obtained with SWNT composites [227].
The morphology of CNTs in polymers depends very much on processing conditions, so as dielectric properties. A transmission electron microscopy (TEM) image for PVDF composite with 2.0 wt% MWNT shows that the MWNT were of uniform spherical particles with a diameter of several micrometers, instead of rope-like structure. However, no distinct MWNTs were observed on the surface, indicating that the MWNTs are wrapped by PVDF. A similar phenomenon has been observed by Jin and Zhang. For the PVDF prepared under the same conditions, however, no spherical particles are seen. This corroborates that the MWNTs are responsible for the formation of the spherical particles. So far, the exact origin of the formation of the spherical particles is unknown. One possibility is that when ultrasonic waves pass through the solution, a large number of microbubbles form, grow and collapse during very short periods of time in a process called ultrasonic cavitations. Theoretical calculations and corresponding experiments suggest that ultrasonic cavitations can generate a local temperature of as high as 5000 K, local pressure of as high as 50.6 MPa, and heating and cooling rates greater than $10^9$ K/s. Under such circumstances, it might be that there is interaction between PVDF molecules and MWNTs. This interaction results in the formation of composites with a spherical substructure by the combination of MWNTs with PVDF. The fact that MWNTs are wrapped by PVDF is indicative of the interaction between PVDF molecules and MWNTs. In order to improve the interaction between PVDF and MWNT and consequently high dielectric permittivity, Dang et al. reported very high dielectric permittivities for functionalized TFP-MWNT/electroactive-polymer nanocomposites using MWNT that was chemically modified with 3,4,5-trifluorobromobenzene (TFBB). The dielectric permittivity can reach 4000 when the volume fraction of TFP-MWNT is 0.15. It is also noted that there is weak temperature dependence of permittivity from 0 to 100 °C for the composite containing 8.0 vol% MWNT. The very high dielectric permittivity originated from the Maxwell–Wagner–Sillars (MWS) effect at percolation, and was attributed to a thin insulating layer of PVDF that was part of the TFP-MWNT. The nomadic charge carriers were blocked at the internal interfaces between the TFP-MWNT and the PVDF, and the large $\pi$-orbital of the MWNT provided the nomadic electrons with large domains. Strongly electrophilic F groups on the TFP-MWNTs further reinforced the MWS effect.

The improved dielectric permittivity was also obtained using other types of conducting fillers with high AR. For example, Sui et al. reported that PP nanocomposite containing 5.0 wt% carbon fibers (CFN) exhibited a surprisingly high dielectric permittivity under wide sweep frequencies and low dielectric loss as well. Its dielectric permittivity was larger than 600 under low frequency, and remained $>200$ at a frequency of 4000 Hz. Wang et al. reported that the conducting PANI nanofibers doped by protonic acids showed a high dispersion stability in P(VDF–TrFE) and led to percolative nanocomposites with enhanced dielectric responses. About a 50-fold rise in the dielectric permittivity of the ferroelectric polymer matrix has been achieved. Percolation thresholds of the nanocomposites are related to the doping level of PANI nanofibers and can be as low as 2.9 wt% for fully doped nanofibers. The interface between the conductive nanofiber and the polymer matrix plays...
a crucial role in the dielectric enhancement of the nanocomposites in the vicinity of the percolation threshold. Compared with other dopants, perfluorosulfonic acid resin is best at improving the performance of the nanofibers in that it serves as a surface passivation layer for the conductive fillers and suppresses leakage current at low frequency.

5.3.3. Effect of 2-demension plate-shape fillers on dielectric properties
Plate-like fillers such as graphite nanoplates are also associated with high dielectric permittivity. PVDF composites of exfoliated graphite nanoplates (xGnP) having dielectric constant up to $4.5 \times 10^2$, have been reported at about 2.4 vol% xGnP loading. In fact, the percolation threshold for the xGnP/PVDF composite system is very low (only about 1.0 vol%), which is of the same order of magnitude as for MWNT/PVDF composites [51]. During the fabrication process graphite nanoplates tend to lie down inside the PVDF matrix. As a result, the faces of the exfoliated graphite nanoplates were parallel to the nanocomposite-film plate. During a hot-press process, several solution-cast films were stacked layer by layer in a “sandwich” form, and then pressed at 200 °C [117]. This promoted the formation of a larger number of microcapacitors in the nanocomposites. As such, the graphite nanoplates were parallel to each other, isolated by a polymer layer as a medium between the nanoflakes. It is believed that the excellent dispersion of exfoliated graphite nanoplates and the existence of many microcapacitors in the PVDF matrix contribute to high dielectric permittivity.

5.3.4. Effect of core–shell fillers on dielectric properties
Fillers with core–shell microstructure are unique and are reported for many years. They could be used in many fields such as catalyzers in chemical industry and novel drugs in biological engineering [232–244]. As discussed in the above sections, the behavior of the dielectric properties of inorganic filler/polymer composites is very complex. Very often, a remarkable improvement in the permittivity is accompanied by an unacceptable dielectric loss due to the use of conducting fillers. To overcome the issue, very recently fillers with core–shell structure have been dispersed into polymers. By tailoring the thickness and characteristics of the core–shell fillers, the integrative dielectric properties of the filler/polymer composites were improved [115,245–247]. Shen et al. [245] reported on a new approach, leading to both extremely stable high-permittivity and low dielectric loss of the polymer dielectrics as shown in Fig. 35. Instead of directly adding dielectric ceramic or conductive fillers, they used core/shell hybrid particles (denoted as Ag@C) with metal Ag cores coated by organic dielectric shells as fillers. The organic dielectric shells not only act as interparticle barriers to prevent Ag particles from direct connection but also produce excellent compatibility between the fillers and the polymer matrix and ensure the dispersion of fillers in the polymer matrix. Furthermore, Shen et al. [246] studied the effect of interfacial layers on the dielectric properties of polymer nanocomposites filled with core–shell structured Ag@C particles. By controlling the process conditions, four kinds of core/
shell Ag@C nanoparticles were employed. The diameters of the silver cores were distributed over 60–110 nm with an average diameter of 80–90 nm. Fig. 36 shows strong dependence of dielectric permittivity, conductivity and dielectric loss of the Ag@C/epoxy composites on the thickness of C-shell layer and the concentration of Ag@C fillers. The use of fillers with thin C-shell layer would result in the high permittivity, low conductivity and low dielectric loss, indicating the significant role of the C-shell layer in improving the dielectric properties of the he Ag@C/epoxy composites. Dang et al. [247] also pointed out the effect of shell-layer thickness on the dielectric properties in Ag@TiO$_2$ core@shell nanoparticles filled ferroelectric PVDF composites. Therefore, it is an important way to adjust the dielectric properties of polymer composites by employing suitable core–shell structure particles. Core/shell nanoparticles with metal cores and dielectric shells are ideal candidates to be used as fillers in percolative composites as illustrated most recently. They provide not only a barrier layer between the conductive fillers but also the possibility of tuning the dielectric properties. Easy processibility of core/shell nanoparticles has paved the way for the application of core/shell nanoparticles in percolative composites [248,249].

Fillers are very important factors to affect the dielectric properties of the polymer composites. In order to acquire the required dielectric properties, it is necessary to choose suitable fillers with
different physical–chemical characteristics. Dielectric properties can also be tuned by changing the concentration of fillers, developing unique filling way (micro–nanosize cofilled) or employing core–shell structure fillers.

6. Effects of measurement conditions on dielectric properties

Dielectric materials are often used in different electromagnetic environments [1,2,4,6]. It is found that many factors have a decisive effect on the dielectric properties of polymer–matrix composites. Within these factors, researchers often play more attention to environmental temperature, measurement frequency and strength of applied electrical field. For new dielectric materials, it is important to develop laws that describe the the variation of dielectric properties on the basis of three crucial factors mentioned above.

6.1. Temperature dependence of dielectric properties

6.1.1. Organic fillers/polymer composites

Polymers are made of a large number of monomer units that are chemically bound together. Macroscopical properties of polymers may change when temperature changes. Therefore, we may explore the effect of temperature on the dielectric properties of polymers and polymer–matrix composites. As a very important dielectric polymer, the change in the dielectric behavior of PVDF, its copolymers and terpolymers is often studied due to their high-permittivity and remarkable electrostrictive strain [19,20,24,28,29,34–37,40–42,64–73,250–253].

For example, P(VDF–TrFE–CFE/CTFE) terpolymers exhibit a very high electrostrictive strain of 4–5% [251,252]. This has been ascribed to their relaxor-like structure [253], similar to electron-irradiated P(VDF–TrFE) copolymers. A typical relaxor linear as well as nonlinear dielectric response has indeed been detected in these polymer systems [254]. Fig. 37 shows a typical relaxor broad dispersive dielectric maximum in the temperature dependence of the real part of the complex dielectric constant ($k$) in the P(VDF–TrFE–CFE) terpolymer. Contrary to ferroelectrics, relaxors do not undergo a symmetry-breaking transition into a long-range ordered state on cooling in zero bias electric field. Rather, only polar nanoregions persist down to the lowest temperatures. Therefore, the dispersive maximum in $k'(T)$ does not denote a phase transition but the result of the fact that $k'$, at a certain temperature that depends on the experimental time scale, starts to deviate from its static value [254,255]. In spite of a relatively large ionic conductivity, it can clearly be seen that values of the dielectric constant in the P(VDF–TrFE–CFE) terpolymer does not exceed 50, and are much lower than those in inorganic piezoelectric systems. However, after conducting PANI (c-PANI) particles at different concentrations are dispersed into the terpolymer matrix by a solution casting process, temperature dependences of $k'$ in the

![Fig. 37. Temperature dependence of $k$ measured at different frequencies in P(VDF–TrFE–CFE) terpolymer. The temperature dependence of the static dielectric constant ($k_s$) measured via charge accumulation technique, is also shown [250].](image)
c-PANI/P(VDF–TrFE–CTFE) is shown in Fig. 38. It can clearly be seen that the addition of cPANI increases the dielectric constant, particularly when the amount of c-PANI approaches the percolation threshold. These two trends are related to the fact that the percolation is approaching [256]. However, o-CuPc/P(VDF–TrFE) composites show a complicated temperature dependence of the dielectric properties, which might be associated with the microstructure of composite and physical characteristics of o-CuPc fillers [257]. For the pure (61/29/10 mol%) P(VDF–TrFE–CFE) terpolymer, the dielectric permittivity and dielectric loss display very small differences during heating and cooling processes. The peak value (near room temperature) of the dielectric permittivity is greater than 50 at 100 Hz [258].

6.1.2. Insulating ceramic fillers/polymer composites

When PLZT [(Pb0.005La0.095)(Zr0.65Ti0.35)O3] ceramic particles are mixed with the P(VDF–TrFE) copolymer, the paraelectric-to-ferroelectric phase transition and β-relaxation were detected [254]. The thermal hysteresis detected during cooling and subsequent heating runs and the typical Curie-Weiss behavior of the dielectric strength. The dielectric response of the PLZT–P(VDF–TrFE) composite is therefore very similar to that observed in the P(VDF–TrFE) copolymer. Although \( k' \) and \( k'' \) values in composite are due to the high values of the dielectric constant of PLZT ceramics which are higher than those in the copolymer, the dielectric relaxation processes of the ferroelectric copolymer dictate the dielectric response of the composite. An increase in the dielectric constant due to the PLZT admixture

Fig. 38. Temperature dependence of \( k' \), measured at several frequencies in cPANI/P(VDF–TrFE–CTFE) composite samples of two different cPANI vol%, (a) \( x = 25.7 \) and (b) \( x = 12.2 \) [250].

Fig. 39. Dielectric constant at 100 Hz and 1 kHz vs. temperature for hot-press composites. For comparison, the dielectric constant of the P(VDF–TrFE) 55/45 mol% copolymer prepared using the same process is also shown in the Fig. [117].
suggests that this composite might present an example of a piezoactive system whose dielectric properties could be relatively easily tuned by changing the PLZT/copolymer ratio [254]. Arbatti et al. [117] reported on novel ceramic–polymer composites with high dielectric permittivity by dispersing CCTO ceramic particles into a P(VDF–TrFE) copolymer. In order to acquire a homogeneous mixture, a multilayer stack of solution-cast films was packed in a “sandwich” figuration during the hot-press process. Temperature dependence of the dielectric behavior of the multilayer composite samples is shown in Fig. 39. Clearly, the dielectric constant reaches its maximum at ca. 70 °C, which is the transformation temperature between the ferroelectric and paraelectric phases for the P(VDF–TrFE) 55/45 mol% polymer matrix. It is well-known that the dielectric constant of PVDF-based ferroelectric polymers at the ferroelectric-to-paraelectric phase-transition temperature is much higher than that at room temperature [257]. Bai et al. [28] reported the temperature dependence of the dielectric permittivity of the 50 vol% PMN–PT/P(VDF–TrFE) composites can be tuned by changing the irradiated dose. Namely, the temperature dependence of the dielectric permittivity of the composites becomes weak with increasing irradiated dose, which is very useful for tuning the dielectric properties of ferroelectric polymer–matrix composites.

In fact, the variation of the dielectric properties of the polymer–matrix composites is very complex due to the effects of fillers with different physical and chemical characteristics. When the insulating fillers are dispersed in polymers, the dielectric permittivity of the resulting composites does not change much with temperature [43,260]. It is likely that the temperature had a weak effect on the physical and chemical characteristics of fillers. When the temperature is changed from −50 to 150 °C, the dielectric permittivity of the BaTiO3/Pi composite films prepared via in situ polymerization exhibits weak temperature dependence [43]. For the sample with 40 vol% BaTiO3, the maximum dielectric permittivity is 19.7, 18.8, 18.5, and 18.4 at 103, 104, 105, and 106 Hz, respectively. According to the X7R EIA specification (EIA = Electronic Industries Association), the permittivity of a capacitor should vary less than ±15% of that at 25 °C in the temperature interval from −55 to 125 °C. In this case, the maximum dielectric permittivity between 20 and 30 °C was regarded as the 25 °C value of the specification. As a result, the calculated relative tolerance of the dielectric permittivity in the temperature range of −50 to 130 °C is 12.3%, 9.5%, 9.9% and 9.5% at 103, 104, 105 and 106 Hz, respectively. However, the variation of the dielectric permittivity of a three-phase (BaTiO3–HA)/PVDF nanocomposites does not support the above explanation [44]. Namely, the dielectric permittivity of the (BaTiO3–HA)/PVDF nanocomposites has a remarkable improvement at about 100 °C. It is likely that the HA phase plays a crucial effect on the dielectric properties of the composite system.

6.1.3. Semiconducting ceramic fillers/polymer composites

When semiconducting particles are employed as fillers, the dielectric permittivity of the polymer composites displays often a remarkable increase [35,45,247,261], which can be attributed to the

![Fig. 40. Temperature dependence of the dielectric permittivity at 1 kHz (a) the volume fraction is 0.21, 0.24, 0.19, and 0.18 for the shell_8, shell_13, shell_60, and shell_120 cases [246]. (b) Temperature dependence of the dielectric permittivity at 1 kHz of the composite films containing Ag@C particles with the thicker shells at different concentrations [245].](image)
conductivity increase of semiconducting fillers with temperature. For example, Dang et al. [35] reported a rescaled temperature dependence of the dielectric behavior of the LTNO/PVDF ferroelectric polymer composites. The PVDF–LTNO composite with high conductivity LTNO ceramic particles also exhibits a high dielectric constant. However, the dielectric loss tangent of this kind of composite is always low. This result could be explained by complicate polarization such as interface polarization interaction appearing between the PVDF and the LTNO phases. It also shows that the dielectric properties of the LTNO/PVDF composites could be tailored by employing LTNO ceramic fillers with different chemical stoichiometric amounts. The results from Dang’s group support this explanation [45,247].

6.1.4. Conducting fillers/polymer composites

Unlike the fillers mentioned above, when metal particles are filled into polymers, the high dielectric permittivity at the percolation concentration often decreases dramatically with an increase in temperature [19], which might be attributed to the inevitable thermal expansion of polymer composites. It is possible that the thermal expansion results in a breakdown of conducting network structure. The decrease in conductivity in the Ni/PVDF composites with temperature supports the effect of thermal expansion. However, when conducting fillers with large aspect ratios, such as CNT and CF, are mixed with polymers, the dielectric permittivity of the fiber-shape fillers/polymer composites increases with increasing temperature. The reason might be that there is chemical bond interaction between fiber-shape fillers and the polymer matrix that blocks the thermal expansion of composites. For practice applications of high dielectric permittivity materials, a weak temperature dependence of dielectric permittivity of the polymer composites is very important. Therefore, how to decrease the temperature dependent instability of dielectric permittivity is a very important challenge. Progresses have been made in this direction. For example, Qi et al. [21] reported that when nanosize Ag particles were dispersed in an epoxy resin, the Ag/epoxy nanocomposites exhibited a high dielectric permittivity (∼300) near the percolation threshold (23 vol% Ag). Furthermore, the dielectric permittivity had higher temperature stability from 25 to 135 °C. The reason would be that the nanosize Ag particles were prepared in the epoxy resin direct (in situ method). As such, the microstructure of the Ag/epoxy resin composites became more resistant to temperature induced structure change. Nan’s group reported on a different method to acquire the temperature stability of dielectric permittivity in metal particles/polymer composites [245,246]. The use of Ag@C core/shell structure particles with a thin (nanosize) organic shell layer, as shown in Fig. 40, resulted in remarkable temperature stability of dielectric permittivity in the Ag@C/epoxy composites. Here the organic nanoshells served as electrical barriers between the Ag cores to form a continuous interparticle-barrier-layer network and to retain a stable high dielectric permittivity and low loss. Obviously, the use of nanosize metal particles and their core–shell structure is efficient at tuning the dielectric properties of the conducting fillers/polymer composites.

6.2. Frequency dependence of dielectric properties

As described in Chapter 2, the variation of dielectric properties of the materials always depends on frequency because different molecule groups and structures have different response characteristics in different frequency ranges. Therefore, the dielectric behavior of the composites consisting of different components may display different frequency dependence.

6.2.1. Organic fillers/polymer composites

Two kinds of organic fillers, CuPc and PANI, are often used to prepare high-κ polymer composites [64–73,75,76,122,250–254,257–259]. CuPc and PANI are organic materials, their composites show excellent flexibility and can be employed as electrostriction materials [64,68,73]. Temperature dependence of the dielectric permittivity in these organic fillers/polymer composites is also strong. For example, Zhang et al. [64] reported that although the dielectric permittivity of the 40 wt% CuPc/P(VDF–TrFE) composites increased significantly compared to polymer matrix, as shown in Fig. 41a, it also depended very strongly on frequency. A simple solution method would be effective at creating strong interaction between CuPc and P(VDF–TrFE).
After the CuPc/P(VDF–TrFE) composite was irradiated, its permittivity was increased, especially at 50 °C as shown in Fig. 41b. However the dielectric permittivity decreased dramatically with temperature. Based on this idea, surface modification of the CuPc particles and chemical graft methods were employed to realize excellent composites. Wang et al. [262] studied a nanocomposite consisting of PVDF as matrix and PCMS grafted with high dielectric constant CuPc (PCMS-g-CuPc) as filler. Compared to the PVDF and CuPc/PVDF composites, the (PCMS-g-CuPc)/PVDF composite displayed a marked increase in dielectric permittivity and a relatively weak frequency dependence of dielectric permittivity. The significant enhancement of the dielectric response can be attributed to an enhanced exchange coupling effect as well as the Maxwell–Wagner–Sillars polarization mechanism. Wang et al. [65,66] also employed P(VDF–TrFE) and P(VDF–TrFE–CFE) as matrices, respectively, to study the effect of graft and blending processes of the CuPc/polymer composites on their dielectric properties. They found that compared with simple blend of the P(VDF–TrFE–CFE) and CuPc, a lower dielectric loss and a higher breakdown field were achieved in the grafted nanocomposite. This could be attributed to a more uniform distribution of o-CuPc particles in the polymer matrix as well as a much smaller inclusion size. Moreover, the dielectric constant of the grafted nanocomposite at frequencies above 1 kHz is much higher than that of the simple blend, indicating an increased interface effect such as the exchange coupling that can enhance the dielectric response.

By employing PU as polymer matrix, Huang et al. [70] reported on fully functionalized high-dielectric-constant nanophase polymers with high electromechanical response. Three-component multifunctional PANI-g-PolyCuPc-g-PU composites exhibit relatively weak frequency dependence. Such a nanophase polymer has a strong interface effect which through exchange coupling markedly increases the dielectric response to an extent that could exceed what would be expected form simple mixing rules for dielectric composites, confirming a recent theoretical prediction [199]. Consequently, these self-organized nanophase polymers exhibited high dielectric permittivities, reduced dielectric losses, and improved breakdown fields and reliability, all of which are highly desirable for high-dielectric-permittivity materials for actuator and dielectric applications.

When the organic conducting particles (PANI) are employed as fillers, the frequency dependence of dielectric properties is often strong [74–76,250]. Bobnar et al. [250] reported on an enhanced dielectric response in all-organic PANI/P(VDF–TrFE–CFE) composite. Although the conductivity at the lowest frequencies approaches the direct current conductivity, the dielectric permittivity and conductivity data are strongly remindful of the dielectric relaxation with the characteristic frequency of $\sim 10^4$ Hz. Maxwell–Wagner effection – the charging of interfaces that occurs in electrically heterogeneous materials by itself leads to dielectric response with the frequency character being identical with that of the Debye dipolar absorption. It is obvious that the pure terpolymer exhibits dielectric properties typical of inorganic relaxors, yet its dielectric constant is much lower. On the other hand, an

Fig. 41. (a) The weak-field (100 V/cm) dielectric permittivity as a function of frequency for the composite (squares) and the polymer matrix (crosses). Data points are shown and solid curves are a guide to the eye [64]. (b) Weak-field dielectric permittivity as a function of the frequency of the irradiated composite film with 40 wt% oligomer CuPc measured at 25 and 50 °C [257].
admixture of PANI, whose conductivity follows the Mott's variable range hopping behavior, strongly increases the dielectric constant of the terpolymer, especially when approaching the percolation threshold. The frequency dependence of the composite's dielectric response is tentatively described in terms of the extended Maxwell–Wagner mixture approach. Wang et al. [74] reported on an enhancement of the electrical properties of ferroelectric polymers by adding polyaniline nanofibers with controllable conductivities. As shown in Fig. 42, the dielectric constant of the PANI–HCl nanofiber (2.9 wt%)/P(VDF–TrFE) composites is 2–4 times higher than that of the polymer matrix at frequencies above 0.1 MHz. The exchange coupling between the nanosized filler and P(VDF–TrFE) with a large difference in dielectric response or inhomogeneous field distribution in the matrix is likely responsible for the observed dielectric enhancement [263].

It is common sense that the difference in the electron work function of the semiconductor and the conductor results in a thin layer in the semiconductor close to the junction which is depleted of mobile electron carriers. When the concentration of conductive PANI nanofibers randomly distributed in the insulating ferroelectric polymer is close to the percolation threshold, the composites are semiconductive and the depletion regions may be located at the interface between the composites and metallic electrodes. The occurrence of the depletion layer is also possible because of the partial overlap of the nanofiber grain boundaries near the percolation threshold. When the PANI was doped with decylbenzene sulfonic acid (DBSA) and perfluorosulfonic acid (PFSA) resin, respectively, the Debye-like relaxation of the PANI–PFSA/P(VDF–TrFE) composite takes place at a lower frequency than that of the PANI–HCl/P(VDF–TrFE) composite and effectively restrains the leakage current of the former. However, in comparison to the PANI–PFSA/PANI composite, the PANI–DBSA/PANI composite presents weak frequency dependence of dielectric permittivity.

6.2.2. Ceramic fillers/polymer composites

All kinds of ceramic fillers were used in order to acquire high-dielectric-permittivity polymer–matrix composites [28–44,108–111]. Frequency dependence of the dielectric permittivity in the insulating ceramic fillers/polymer composites is relatively weak. The high-$k$ of the composites is mainly from
interface polarization and the high dielectric permittivity of ceramic fillers themselves, which have weak frequency dependence. The slow decrease in dielectric permittivity might be related to the high-frequency dielectric relaxation. For example, Kuo et al. [108] reported on the frequency dependence of the dielectric properties for the BaTiO$_3$/epoxy composites in the bulk form with different heat treated ferroelectric ceramic fillers. The dielectric permittivity slightly decreases and the dielectric loss slightly increases as the test frequency increases. It is has been reported that the loss tangent values are high at low frequencies up to 1 kHz and are very low at frequencies from 10 kHz to 1 MHz. The dielectric losses increase again at frequencies higher than 1 MHz. The behavior of the dielectric loss at low frequencies below 1 kHz is attributed to the domain motion and inhomogeneous conductivity, and that at frequencies above 1 MHz to the domain-wall motion. Dang et al. [29,43] reported that the dielectric permittivity of the BaTiO$_3$/PVDF composites was weakly frequency dependent. If the BaTiO$_3$/PI nanocomposite was prepared by in situ polymerization, the frequency dependence of the dielectric permittivity could be further decreased. This is because the in situ polymerization process can ensure the strong interfacial interaction between nanosize BaTiO$_3$ particles and polymer chains.

When semiconducting ceramic fillers are used to prepare polymer composites, their dielectric permittivity improves markedly due to very high dielectric permittivity and relatively high conductivity of the ceramics [37,45,264]. However, in most cases a remarkable frequency dependence of dielectric properties can be observed. For example, Dang et al. [37] reported that the dielectric permittivity reaches about 150 when the volume fraction of LTNO is 0.30 in the LTNO/PVDF composite. However, the dielectric permittivity and dielectric loss depends strongly on temperature. For the CCTO/PI hybrid films, when the concentration of CCTO is lower than 20 vol%, the permittivity of the hybrid film does not change with an increase in frequency. However, when the concentration of CCTO is 30 vol%, the permittivity has a weak dependence on frequency [45]. An obvious frequency dependence of the dielectric permittivity can be observed when the concentration of CCTO is more than 40 vol%. Namely, the permittivity decreases dramatically with an increase in frequency. This phenomenon could be also ascribed to the semiconductive characteristic of the CCTO filler. Arbatti et al. [117] reported the dielectric spectra of the hot-press multi-layer composite samples at room temperature, as shown in Fig. 43. The dielectric constant increases with the initial number of layers used in the hot press and then levels off with a further increase in that number. For example, the difference in the dielectric behavior between four-layer and six-layer composites is very small. The Cole–Cole plot for the dielectric behavior of the composites at room temperature is shown in Fig. 43b. In addition to the major dielectric relaxation process, a low-frequency process was observed at the low-frequency end (left-up end of the curve), which is responsible for the dielectric loss obtained at low frequency. This low-frequency process can be caused by the conductive behavior of the composites or the relaxation process caused by the heterogeneous nature of the composites (heterogeneous relaxation).

![Fig. 43](image-url) (a) Dielectric constant vs. frequency from 100 Hz to 1 MHz for the composites at room temperature. (b) Cole–Cole plot of the dielectric behavior for the hot-press composites at room temperature. The dotted lines are the fitted results using the Cole–Cole equation [117].
6.2.3. Conducting fillers/polymer composites

Many research works have proven strong frequency dependence of dielectric permittivity in conducting fillers/polymer composites [19–25,58,61,72–77,265,266]. Namely, the low-frequency dielectric permittivity and dielectric loss are high in the composites, which would be attributed to the crucial electrode polarization and low-frequency leakage current. For example, Panda et al. [265] reported on weak frequency dependence of nanocrystalline Ni/PVDF composites over the whole frequency range when the volume fraction of Ni was 0.25. When its concentration approaches the percolation threshold, the variation of permittivity with frequency is more pronounced. When conducting xGnP were dispersed in PVDF to form the xGnP/PVDF nanocomposites, the obvious frequency dependence of permittivity was also reported [49], which followed the same law as for the use of CNF [123] and CNT [50,51] as conducting fillers. In order to reduce the frequency dependence of the conducting fillers/polymer composites, three-component (ceramic filler–conducting filler)/polymer composites are designed [20,54,57,59,61,68,27,204,209]. For example, Dang et al. [20] reported that the frequency dependence of dielectric permittivity was weakened when insulative ceramic BaTiO3 and conducting Ni particles were mixed with PVDF together. Moreover, the (Ni–BaTiO3)/PVDF composite had a low conductivity even if at low frequency (100 Hz). Another way to decrease the frequency dependence of permittivity is to use core–shell structure particles, which has been proven to be effective method [245,246]. For example, Nan’s group studied percolative nanocomposites using core/shell-structured particles as fillers. The Ag cores were coated with organic carbonaceous shells (denoted as Ag@C). The matrix is an epoxy resin. The thickness of the organic carbonaceous shell has a very significant effect on the frequency dependence of the permittivity of the Ag@C/epoxy composite. The results of Dang’s group also confirm that the Ag@TiO2 core–shell particles with thin TiO2 layer results in the weak frequency dependence of dielectric permittivity and dielectric loss in the Ag@TiO2/PVDF composites [247]. These results suggest that the strong frequency dependence of the dielectric properties in conducting fillers/polymer composites can be lowered by changing the composition of composites and employing the core–shell structure particles.

6.3. Electrical field dependence of dielectric properties

As introduced in Section 2.4, high-k polymer composites are often used as electric energy dielectric materials. As shown in Eq. (9), the maximum energy storage density \( w_{\text{max}} \) of materials is directly proportional to the dielectric permittivity and the square of the breakdown field. It is very desirable if the polymer composites possess high dielectric permittivity and high breakdown field. It is well-known that the dielectric permittivity of a material is relative to its electrical polarization. This drives us to employ a strong electrical field to induce strong electrical polarization. However, the electrical field is not stronger than the breakdown field of the material. As dielectric polymer composites, we should investigate the electrical field dependence of the dielectric properties of inorganic/polymer composites. Very recently, numerous studies have addressed this issue [12,64,67–70,73,245,246,251,254,257]. Additionally, the high dielectric permittivity also helps to induce large electrostriction of the polymer composites [64,67–70,73,252,254,257].

Zhang’s group reported on an electrical field induced high dielectric permittivity in the 40 wt% CuPc/P(VDF–TrFE) composite prepared via a simple solution process [64]. The maximal dielectric permittivity value reaches 450 at 10 kV/mm while only 220 without electrical field. The high dielectric permittivity, therefore, contributes greatly to the electrical strain as shown in Fig. 44 [64]. Nan et al. [245] shows that the applied electrical field does not significantly improve the dielectric permittivity in the core–shell Ag@C/epoxy composites (Fig. 45a). However, the \( I–V \) characteristic of this composite displays obvious electrical field dependence (Fig. 45b). A strongly nonlinear \( I–V \) relationship is observed only in the composites where the volume concentration of fillers exceeds the percolation threshold. Wang et al. [74] showed that the applied field had a significant effect on electrical polarization of the PANI/P(VDF–TrFE) composites. Moreover, the polarization depends very much on the doping composition in PANI. Hysteresis loops are typical characteristics of ferroelectric materials. P(VDF–TrFE) nanocomposites with 2 wt% of PANI–HCl nanofibers display polarization hysteresis, which gradually expands with increasing field. For the current composite, however, the breakdown field still falls in the range to afford significant electromechanical response. Huang et al. [72] confirm
that PANI/P(VDF–TrFE–CTFE) composites with high dielectric permittivity near the percolation concentration of PANI fillers exhibit a large electrostriction strain under low applied electrical field. They also prepared fully functionalized high-dielectric-permittivity nanophase polymers with high electromechanical responses [70], which is very high compared with other types of electroactive polymers [267,268]. The longitudinal or thickness strain is a $\frac{\Delta L}{L_0}$ strain induced under 27 kV/mm, which is currently a very high strain value. However, it is lower that what is expected from the result [86]. In fact, recent works show that the improvement of dielectric permittivity is not the sole method to acquire a large electromechanical strain [86] and high electric energy storage density [269]. Carpi and Rossi reported that after TiO$_2$ powder was dispersed into a silicone dielectric elastomer, the dielectric permittivity increased very slowly with increasing concentration in TiO$_2$. However, the increase in the applied electric field can induce a surprisingly high electromechanical strain. Zhang et al. also reported that nanocomposites of ferroelectric polymers with TiO$_2$ nanoparticles exhibited significantly enhanced electrical energy density [269]. When the volume concentration of TiO$_2$ nanoparticles increases, the dielectric permittivity of the TiO$_2$/P(VDF–TrFE–CTFE) composites and the TiO$_2$/P(VDF–CTFE) composites shows very weak field dependences as shown in Fig. 46a. On the other hand,

![Fig. 44](image-url)

Fig. 44. (a) Dielectric properties of the composites as a function of the applied-field amplitude for the composite with 40 wt% CuPc. (b) The strain amplitude as a function of the applied-field amplitude measured at room temperature. The applied-field frequency is 1 Hz. Crosses are the data and the solid curve is a guide to the eye. For comparison, the strain from the electrostrictive P(VDF–TrFe) copolymer at the same field range is also shown (the dashed curve) [64].

![Fig. 45](image-url)

Fig. 45. (a) Bias dependence of dielectric permittivity at $10^3$ Hz of the composite films containing Ag@C particles with the thicker or thinner shells. (b) $I$–$V$ characteristics of these composite films, where the inset shows repeated measurements to the $I$–$V$ behavior of the 24 vol% Ag@C/epoxy composite with the thicker shells [245].
the electric energy density of the composites displays remarkable field dependence (see Fig. 46b). Namely, the electric energy density of the composites increases with the applied field.

7. Applications for high-k PMCs

High-k polymer composites have a promising wide range of applications in microelectronics, electrical engineering, biomedical engineering, etc., due to their electromechanical response. In what follows, we give outlines of these applications and expect that new applied fields will be developed in the future.

7.1. Applications in microelectronic field

Recently high-k materials have received increasing interest due to various potential applications such as gate dielectrics, high charge-storage capacitor and electroactive materials [17–33,270–274]. Fig. 47 schematically shows an example of realization of embedded passive technology by integrating resistor and capacitor films into laminate substrates [275]. By removing these discrete passive components from the substrate surface and embedding them into the inner layers of substrate board, embedded passives cannot only provide the advantage of size and weight reduction, but also have many other benefits such as increased reliability, improved performance and reduced cost, which have driven a significant amount of effort during the past decade for this technology. However, embedded passive technology has not been commercialized for electronic packages yet due to materials and process issues. Therefore, it is necessary to develop materials that satisfy the requirements of fabrication.
as well as electrical and mechanical performances to enable embedded passive technology to be commercialized. Materials challenges include dielectrics with $k$ above 1000 and low dielectric loss. A very low dissipation factor is desired for radio frequency applications to avoid signal losses. However, much higher values can be tolerated for decoupling applications.

Ceramics are traditionally used high-$k$ materials for capacitor applications. However, they also have many prominent disadvantages. They either require expensive tools or cannot be easily implemented over large PCB substrate areas. Moreover, high temperature annealing or sintering (>500 °C) is often needed to improve the quality of deposited ceramic dielectric films. Such a high temperature annealing process will destroy the organic PCB board, as the organic board needs to be

Table 5
Summary of high-$k$ ferroelectric ceramic/polymer composites candidates for embedded capacitor application.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Dielectric permittivity</th>
<th>Dissipation factor</th>
<th>Filler size</th>
<th>Filler loading (vol%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$/epoxy</td>
<td>40 (1 Hz)</td>
<td>0.035</td>
<td>100–200 nm</td>
<td>60</td>
<td>[279]</td>
</tr>
<tr>
<td>PZT/PVDF</td>
<td>50</td>
<td>20 µm</td>
<td>50</td>
<td>[116]</td>
<td></td>
</tr>
<tr>
<td>PMN–PT/P(VDF–TrFE)</td>
<td>200 (10 kHz)</td>
<td>0.1 (10 kHz)</td>
<td>0.5 µm</td>
<td>50</td>
<td>[28]</td>
</tr>
<tr>
<td>Bimodal BaTiO$_3$/epoxy</td>
<td>90 (100 kHz)</td>
<td>0.03 (100 kHz)</td>
<td>916 nm + 60 nm</td>
<td>75</td>
<td>[253]</td>
</tr>
<tr>
<td>PMN–PT + BaTiO$_3$/epoxy</td>
<td>150 (10 kHz)</td>
<td></td>
<td>900 nm/50 nm</td>
<td>85</td>
<td>[280]</td>
</tr>
<tr>
<td>BaTiO$_3$/P(VDF–HFP)</td>
<td>37 (1 kHz)</td>
<td>&lt;0.07 (1 kHz)</td>
<td>30–50 nm</td>
<td>50</td>
<td>[281]</td>
</tr>
<tr>
<td>CCTO/P(VDF–TrFE)</td>
<td>243 (1 kHz)</td>
<td>0.26 (1 kHz)</td>
<td>50</td>
<td>[117]</td>
<td></td>
</tr>
<tr>
<td>CCTO/PI</td>
<td>49.1 (1 kHz)</td>
<td>0.2 (1 kHz)</td>
<td>1–4 µm</td>
<td>40</td>
<td>[45]</td>
</tr>
<tr>
<td>LTO/PVDF</td>
<td>90 (1 kHz)</td>
<td></td>
<td>40</td>
<td>[37]</td>
<td></td>
</tr>
</tbody>
</table>

Table 6
Summary of high-$k$ conductive filler/polymer composites candidates for embedded capacitor application.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Dielectric constant</th>
<th>Dissipation factors</th>
<th>Filler size</th>
<th>Filler loading</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag flake/epoxy</td>
<td>1000 (10 kHz)</td>
<td>0.02 (10 kHz)</td>
<td>1.5 mm</td>
<td>11.23 vol%</td>
<td>[245]</td>
</tr>
<tr>
<td>Ag@C/epoxy</td>
<td>&gt;300 (1 kHz)</td>
<td>&lt;0.05 (1 kHz)</td>
<td>80–90 nm</td>
<td>25–30 vol%</td>
<td>[282]</td>
</tr>
<tr>
<td>Al/epoxy</td>
<td>105 (10 kHz)</td>
<td>0.02 (10 kHz)</td>
<td>3 mm</td>
<td>80 wt%</td>
<td>[20]</td>
</tr>
<tr>
<td>Ni–BaTiO$_3$/PVDF</td>
<td>300 (10 kHz)</td>
<td>0.5 (10 kHz)</td>
<td>Ni: 0.2 mm</td>
<td>Ni: 23 vol%</td>
<td>[283]</td>
</tr>
<tr>
<td>Ni–BaTiO$_3$/PMMA</td>
<td>150 (1 MHz)</td>
<td>Ni: 4 mm</td>
<td>BaTiO$_3$: 1 mm</td>
<td>Ni: 12 vol%</td>
<td>[284]</td>
</tr>
<tr>
<td>CB/epoxy</td>
<td>13,000 (10 kHz)</td>
<td>3.5 (10 kHz)</td>
<td>30 nm</td>
<td>15 vol%</td>
<td>[285]</td>
</tr>
<tr>
<td>Al–Ag/epoxy</td>
<td>160 (10 kHz)</td>
<td>0.045 (10 kHz)</td>
<td>Al: 3 mm</td>
<td>Al: 80 wt%</td>
<td>[21]</td>
</tr>
<tr>
<td>Ag/epoxy</td>
<td>300 (1 kHz)</td>
<td>0.05 (10 kHz)</td>
<td>40 nm</td>
<td>22 vol%</td>
<td>[22]</td>
</tr>
<tr>
<td>Ag-CB/epoxy</td>
<td>2260 (10 kHz)</td>
<td>0.45 (10 kHz)</td>
<td>Ag: 13 nm</td>
<td>Ag: 3.7 vol%</td>
<td>CB: 30 wt%</td>
</tr>
</tbody>
</table>

Fig. 48. Metal–insulator–metal (MIM) capacitor fabrication processes using ECFs on PCBs. (a) ECF lamination on a PCB substrate, (b) releasing film removal, and (c) top electrodes deposition by a sputtering method [33].
processed under 250 °C. On the other hand, polymers have low cost and can be easily and compatible PCB process whereas their dielectric permittivity typically is low. Polymer–ceramic nanocomposites may have the potential to introduce high dielectric constant with low temperature thick-film fabrication process, because they can combine the advantages of high dielectric constant from the ceramic part and good processibility from the polymer part. Because of the combined advantages of polymer–ceramic composites, they have been subjected to extensive research and have been selected as a major material candidate for the development of embedded capacitors inside organic substrates [276,277].

In most cases even at very high filler concentrations the dielectric constant of polymers does not exceed above 100. For embedded capacitor technology polymer composites should have a dielectric constant of 50–200 to make layout area small enough for embedded capacitors in many cases such as for decoupling. To achieve dielectric constants above 50, high filler loadings around 60 vol% have to be used, which drastically deteriorates the peel adhesion strength and thermal stress reliability of the high-\(k\) composites, inhibiting their real application as an embedded capacitor dielectric. To make the high-\(k\) composites useful, a lower volume filler loading (<50 vol%) has to be used, but this in turn will reduce the dielectric constant of the composites. Therefore, fundamental understanding of the adhesion and thermal stress reliability of dielectric films needs to be addressed in order to obtain high dielectric permittivity (\(k > 50\)) embedded capacitor dielectrics that can successfully pass the adhesion and thermal stress reliability tests.

While ceramic/polymer composites have shown some successful commercial applications, the dielectric permittivity of ceramic/polymer composites is not sufficiently high (\(k < 100\)) for many applications in the next generation electronics [1–4]. To address this issue, disruptive innovation on polymer high-\(k\) composites has also been explored. An approach showing good potential is the high-\(k\) polymer-conductive filler composites based on percolation mechanism. According to scaling theory, high dielectric permittivity can be obtained when the actual filler loading is very close to the percolation threshold [18–23,50–60,68,72–75,188,212,278]. Because the filler loading used in the percolative composites is lower than ceramic/polymer composites, better material processibility and adhesion strength can be expected. However, due to its percolation nature, the electric and dielectric properties of a percolative composite are very sensitive to the composition. A slight change in the composition will lead to a significant change of materials properties, which impose serious challenge of producing materials with reproducible properties. In addition, the dielectric loss (\(\tan \delta\)) of a percolative composite usually is high, which is not desirable for high frequency applications. In order to apply percolative systems for manufacturing of capacitors, fundamental understanding of the dielectric loss of the polymer-conductive filler composites needs to be obtained, and a viable method to obtain a percolative composite with reproducible high dielectric constant and low dielectric loss needs to be developed. Here high-\(k\) ferroelectric ceramic/polymer composites and high-\(k\) conductive filler/polymer composites candidates for embedded capacitor application are summarized in Tables 5 and 6.

Now let us to show how to prepare embedded capacitors with examples. Cho et al. [33] reported on the fabrication of embedded capacitor films (ECF) using a comma roll coater. Compared with a spin coating process for the deposition of BaTiO\(_3\)/epoxy composite films, the comma roll coating method has advantages such as no waste of materials, good coating thickness uniformity, and high productivity. The ECF coated on the releasing film was dried sequentially before rewinding. As an example,

![Fig. 49. Principle of dielectric elastomer generators: (a) dielectric elastomer stretched (charge at low voltage) and (b) dielectric elastomer contracted (charge at high voltage).](image)
using BaTiO$_3$/epoxy composite ECFs, metal–insulator–metal (MIM) capacitors were fabricated on PCB. The capacitor fabrication process is shown in Fig. 48. Kakimoto et al. [3] also reported on ceramic/polymer nanocomposites based on new concepts, which could be developed for embedded capacitor applications. The dielectric constant was above 80 at 1 MHz and the specific capacitance was as high as 8 nF/cm$^2$. By use of this nanocomposite, multilayer printed wiring boards with embedded passive components were fabricated for prototypes.

7.2. Applications in electrical engineering field

High-$k$ polymer composites as one of novel functional materials have a great potential application in electrical engineering. For example, high elastic rubber–matrix composites with high dielectric permittivity are attracting great attention due to their easy, low-temperature processing and flexibility, especially in electrical engineering application such as potential cable accessories [85,263,286–291]. This is because they could balance the distribution of electric field of cable termination to prevent the cable from failure, as shown in Fig. 3. In this field, one has to explore flexible rubber–matrix composites with high dielectric permittivity (>100) and low dielectric loss (<0.05). Up to now, it is difficult to obtain flexible two-component rubber–matrix composites that meet all properties mentioned above when single functional filler is employed. For example, one has to increase the concentration of ceramics in order to improve the dielectric permittivity of two-component rubber–matrix composites. This results in a concomitant decreases in their elasticity [287]. However, conducting fillers, such as metal, carbon black, carbon fiber, and carbon nanotube are used, the dielectric permittivity of the composites increases remarkably when the concentration of conducting fillers is close to the percolation threshold. In this case, the dielectric loss of the composites always increases dramatically and their resistivity decreases sharply. Therefore, the resolution of the problems above is essential if flexible rubber–matrix composites are applied as electric cable accessories. Based on this viewpoint, Dang et al. [61] reported high-dielectric-permittivity three-component high-elasticity nanocomposites with low percolation threshold and low dielectric loss.

Electrical energy storage plays also a key role in mobile electronic devices, stationary power systems, hybrid electric vehicles, and pulse power applications [292,293]. In particular, there is a growing need for capacitors that can accumulate a large amount of energy and then deliver it nearly instantaneously. This kind of “pulse power” is needed for a variety of military and commercial applications. Over time, these applications demand ever higher energy and power densities as well as higher rate capability [294]. Barber et al. [294] showed a complication of reported and calculated energy densities from the literature for the ceramic/polymer composites. However, the results cannot give enough guidance for practical application.

A new application for dielectric elastomers with high dielectric permittivity is to produce power energy because dielectric elastomers can be run in reverse of their usual actuator operation to implement mechanical-to-electrical transition. In the generator mode of operation, charges are placed on the elastomer film in the stretched state. Upon contraction, the increase in thickness of the elastomer increases the separation of opposite charges, and the decrease in planar area compresses like charges. Both changes increase the voltage of the charge, and hence increase the stored electrical energy. Dielectric elastomer generator films have shown very good performance with a generator energy density of up to 0.4 J/g. More importantly, dielectric elastomers have unique advantages compared with competitive electromagnetic generators. In particular, dielectric elastomers have excellent low and variable frequency response, and together with their high energy density are well suited for direct drive designs that eliminate the need for costly and complicated transmissions. Fig. 49 illustrates the elementary generator mode of dielectric elastomers.

Dielectric elastomers (DEs) can be used for traditional point generator applications as a direct replacement for electromagnetic generators. A dielectric elastomer generator can be coupled to an internal combustion engine to make a fuel-powered generator, for example. For these traditional point generator applications, dielectric elastomers may offer advantages such as lower cost, lighter weight, or smaller size. However, for traditional high frequency, point generator applications, dielectric elastomer generators are a new technology competing against a mature one (electromagnetics) that is well suited for the task. Hence, the competitiveness of the dielectric elastomers in these traditional
high frequency applications may depend a great deal on the specifics of the application. It is worthy noting that dielectric elastomers can be made in large area sheets with high performance. Even when not packaged in a sheet form, dielectric elastomers use potentially low-cost materials. These capabilities suggest that dielectric elastomers may be well suited for harvesting energy from large area, distributed power sources such as wind and wave energy.

7.3. Applications in biomedical fields

High-k PMC can act as electromechanical transducers that convert or transduce electrical energy to mechanical energy. In an actuator mode, these transducers convert electrical to mechanical energy, whereas in a generator mode they perform the reverse function and convert mechanical to electrical energy. Flexible electroactive polymers (EAPs) can behave as actuators, changing their shape in response to electrical stimulation. EAPs that are controlled by external electric fields—referred to here as field type EAPs—include ferroelectric polymers, electrostrictive polymers, dielectric elastomers and liquid crystal polymers. Field-type EAPs can exhibit fast response speeds, low hysteresis and strain levels far above those of traditional piezoelectric materials[252,253,268,295,296] with elastic energy densities even higher than those of piezoceramics. However, these polymers also require a high field (>70 V mm) to generate such high elastic energy densities (>0.1 J/cm³). Zhang et al.[64] developed a new class of all-organic field-type EAP composites, which can exhibit high elastic energy densities induced by an electric field of only 13 V/µm. The composites can exhibit high net dielectric constants while retaining the flexibility of the matrix. These all-organic actuators could find applications as artificial muscles, ‘smart skins’ for drag reduction, and in microfluidic systems for drug delivery[297]. Colloquially referred to as ‘artificial muscles’, actuators based on dielectric elastomers are uniquely suited to orthotic and prosthetic development in biomechanics due to their rough similarity in function to natural muscle[298].

Based on the electrostriction of the high-k polymer materials, Xu et al.[299] studied the performance of micromachined unimorph actuators (polymer micromachined actuator PMAT) based on an electrostrictive P(VDF–TrFE) copolymer. Because of the high electrostrictive strain and high elastic energy density (~1 J/cm³) of the active polymer, the PMAT exhibits a very high stroke level with high load capability and high displacement voltage ratio. At the same time, they also reported on an electroactive ceramic/polymer hybrid actuation system for enhanced electromechanical performance[300]. Xia et al.[301] reported an electroactive polymer based microfluidic pump, which was realized by integrating a nozzle/diffuser type fluidic mechanical-diode structure with the polymer microactuator. Additionally, Ren et al.[302] developed a compact electroactive polymer actuator suitable for refreshable Braille display. The compact polymer actuator was developed utilizing the electrostrictive terpolymer, which is suitable for full page Braille display and graphic display. Key issues related to the reliability of electroactive polymers used in the compact actuators and for the mass fabrication of these polymer actuators were investigated. The recent results demonstrate that the EAP Braille actuator meets all the functional requirements of actuators for refreshable full Braille display, which offers compact size, reduced cost and weight. However in 2000, a wheel-based Braille display was reported which can significantly reduce the number of actuators to move

![Fig. 50. Outlook for applications of the high-k polymer composite.](image-url)
the dots in a refreshable display and hence, can reduce the cost of the Braille display markedly [303].

Pelrine et al. [304] also reported on high-strain actuator materials based on dielectric elastomer. Upon applying a voltage, the active portion of the elastomer expands and the strain can easily be measured optically. The active portion expands when voltage is applied and the strain is easy to measure optically. Kofod et al. [305] presented energy minimization for self-organized structure formation and actuation. Here we must stress if the suitable structure to actuators is designed, the flexible actuators can be made into microfluidic pump behaving as ‘artificial heart’, which can be used in biomedical field.

Generally speaking, the high-\( k \) polymer composites have a resplendent outlook from the work reported in this review. The significant strides have been made in the development of polymer composites with greater energy storage capacity, higher energy density and other excellent characteristics. Of course, due to the limitation of this review, we cannot show full applications of the high-\( k \) polymer composites. A simply outlook for applications of the high-\( k \) polymer composites is shown in Fig. 50.

8. Concluding remarks and future perspective

The present paper provides a review on the fundamentals, processes and applications of high-\( k \) polymer–matrix composites. The concluding remarks are as follows:

(1) Existing theoretical models for predicting the dielectric properties of polymer–matrix composites are presented. None of them explains, describes and/or predicts reasonably well the current results due to complexities in microstructure and composition of such composites. For a given composition, the dielectric properties can be significantly different, depending on the preparation process employed.

(2) Interfaces between inorganic fillers and polymers are crucial. Appropriate surface modification of inorganic fillers can improve their compatibility with polymers. Inclusion of core–shell structure fillers is also an important way to promote interfacial interactions between filler and polymer and dispersion of the fillers in the polymers. This improves the dielectric permittivity of the composites. Better filler–polymer compatibility also improves the stability of the micro-structure of the composite and increases the specific surface area of the filler. It may also minimize defects or voids in the composite that can deteriorate the breakdown strength and thus the overall energy density [294].

(3) Ceramic/polymer composites often have the advantage of exhibiting weak frequency and temperature dependence of dielectric permittivity. However, their dielectric permittivity is often low even if a high loading of ceramic particles is incorporated. Moreover, the breakdown strength is weak if ceramic particles are not surface treated.

(4) Conducting fillers/polymer composites display high dielectric permittivity near the percolation threshold. The variation in dielectric permittivity of such composites is very sensitive to the concentration of conducting fillers. It is also sensitive to temperature due to thermal expansion. Three-phase composites consisting of ceramic particles, conducting filler and polymer can be good candidates for acquiring good dielectric properties as well as other characteristics.

(5) The size, shape and concentration of fillers have important effects on dielectric properties. However, the effects of the size and shape of fillers have yet been explored to a sufficient degree. High-\( k \) polymer composites with weak frequency/temperature dependence are crucial for practice applications. Good solutions are still not available for effectively tuning the frequency/temperature dependence of the dielectric permittivity of polymer–matrix composites.

(6) Many studies have been carried out on the use of high-\( k \) polymer composites as dielectric layers in embedded capacitors and pulse power energy storage capacitors. Flexible high-\( k \) polymer composites can also be used as biomedical devices owing to their great electrical mechanical response.
Based on the state of the art, future perspectives are as follows:

1. It is necessary to refine existing models or develop new ones for dielectric composites.
2. Much more attention should be paid to nanosize fillers. They may create much higher amounts of polymer–filler interfaces and consequently generates much more significant polarization than microsize ones. Controlled dispersion of nanofillers is a very challenging issue [306].
3. It is worthwhile to explore the synergy between different types of fillers and the potential of core–shell fillers in order to attain high-\(k\) polymer composites with other excellent properties [307,308]. Surface design and modification of fillers are a very important issue.
4. It is important to develop high-\(k\) materials with weak frequency/temperature dependence of dielectric permittivity, especially when they are used in special environment [309].
5. Fabrication of electronic devices with high-\(k\) polymer composites can be very interesting as it can significantly reduce their weights and volumes. High-\(k\) polymer composites may also find applications in biomedical field.

Acknowledgements

This work was financially supported by NSF of China (No. 50977001, 51073015), the Ministry of Sciences and Technology of China through 863-Project (No. 2008AAA03Z307), the Ministry of Sciences and Technology of China through China-Europe International Incorporation Project (No. 2010DFA51490), State Key Laboratory of Power System (No. SKLD09KZ03), State Key Laboratory of Electrical Insulation and Power Equipments (No. 09ZQ01), Program for New Century Excellent Talents in University (NCET), and the Fundamental Research Funds for the Central Universities (No.06103012, 06103011).

References


Z.-M. Dang et al. / Progress in Materials Science 57 (2012) 660–723


