Study of the effective dielectric constant of lead-free electroactive polymer-piezoceramic composites using theoretical models

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The effective dielectric constant of electroactive polymer–piezoceramic composites is studied using various theoretical models. The lead-free piezoceramic $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) which has interesting dielectric and piezoelectric properties is chosen as the filler in different polymer matrices such as Polyvinylidene fluoride (PVDF):$Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT), Polyvinylidene fluoride-trifluoro ethylene, P(VDF-TrFE):BCZT, and Nylon 11:BCZT. The effective dielectric constant depends on the polymer, and filler characteristics such as its size, shape, volume fraction, and its interaction in the electroactive polymer matrix which is studied in the present article using theoretical models. The effect of filler volume percentage (10–40 vol%) on the dielectric constant is studied, and results are discussed. It is found that P(VDF-TrFE): BCZT composites at 40 vol% exhibited a higher effective dielectric constant (ε_r = 120) compared to PVDF: BCZT (ε_r = 77) and Nylon11: BCZT composites (ε_r = 56). Study indicates the effectiveness of the theoretical models in predicting the polymer composite properties and help in designing the best performing composites for non-linear optics (NLO), energy storage, and energy harvesting applications.

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1. Introduction

Polymers are broadly classified into polar and non-polar polymer groups. Among these, polar polymers draw more attention due to the presence of permanent electrical dipoles and exhibit a comparatively higher dielectric constant than nonpolar polymers [1,2]. The polar polymers are electroactive in nature and known as electroactive polymers (EAPs) or ferroelectric polymers. EAPs are also flexible and lightweight as desired in many applications. Examples of EAPs are Polyvinylidene fluoride (PVDF) (β and γ–phases), PVDF combined with trifluoroethylene (TrFE) [P(VDF-TrFE)], Poly(vinylidene fluoride-co-hexafluoropropylene [P(VDF−HFP)], Poly(vinylidene fluoride-*co*-chlorotrifluoroethylene [P(VDF−CTFE)], and odd-numbered Nylons (*α* and *γ* phases of nylon-11) [2, 3]. The above said EAPs have been considered for the different applications, such as strain/stress sensors, transducers, flexible actuators, ultrasound scanners for medical imaging, infrared (IR) sensors, energy harvesters, and high-density memory devices [1–3].

PVDF polymer exists in five different phases, namely, α-, β-, γ-, δ-, and ε-phases, based on different chain confirmations. Among the different types of PVDF, α-phase is nonpolar, whereas in δ-, γ-, and β-phases, polymer chains possess net permanent dipoles. In these α and β phases are stable and most commonly formed in the common synthesis methods, whereas γ-, δ-, and ε-phases are difficult to obtain through conventional methods [3, 4]. The structure of α- phase PVDF has a trans-gauche conformation (TGTG′), and hence it is non-polar. In the β-phase, the dipole moment of the two F-C and two C-H bonds adds up in such a way that the monomer gets an effective dipole moment in the direction perpendicular to the carbon backbone, i.e., it arranges into a planar TTTT (all trans) zigzag chain conformation. Therefore, the β-phase results in a high dielectric constant as well as high electroactive properties [3, 4]. Further, to enhance and stabilize the electroactive phase of PVDF, copolymers like P(VDF-TrFE) were studied. Where randomly distributed VDF and TrFE units form the co-crystalline phase throughout the compositional range of the copolymers, the larger proportion of bulky trifluorine atoms in PVDF prevents the molecular chains from adopting the tg+tg− conformation. This stabilizes copolymers into a ferroelectric phase with the extended planar zigzag (all-trans) conformation at room temperature, whose crystalline phase is comparable to the β phase of the PVDF polymer [2,3]. Another group of EAPs is polyamides, which are commonly known as nylons. In this context, Nylon 11 is quite interesting, due to an odd number of long carbon-chain amide repeating units, unlike other conventional polyamides. Moreover, nylon-11 possesses high impact strength, good resistance to hydrolytic reagents, low melting temperature, and good piezoelectric and pyroelectric properties [4].

However, all EAPs mentioned above exhibit low dielectric constant (ε_r = 5 - 20) and low piezoelectric properties compared to the piezoceramics, like lead-free ferroelectric ceramics: $BaTiO_3$, $K_{0.5}Na_{0.5}NbO_3$ (KNN),

$Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) where ε_r>100 [5, 6]. In order to improve the dielectric and piezoelectric properties of the EAPs, composites are studied by incorporating ferroelectric ceramic particles as fillers at different volume percentages in the polymer matrix [2 – 4]. Bharathi et al. fabricated PVDF with KNN nano/microparticle composites and studied the size-dependent dielectric and piezoelectric properties [7]. The results showed that PVDF with KNN microparticle composites exhibited a high piezoelectric constant of 35 pC/N at a ceramic volume percentage of 70 vol%. Whereas, PVDF with nanoparticle composites exhibited a high dielectric constant value of around ε_r = 3273 at 100 Hz for 40 vol% [7]. Similarly, Kobayashi et al. studied the dielectric properties of PVDF-$BaTiO_3$ composite films and showed that ε_r=31.8 at 30 vol% $BaTiO_3$ with high capacitance density as large as 0.63 nF/mm^2. Therefore, it is important to understand and study the polymer-ceramic interaction and other factors influencing the properties of polymer composites using suitable theoretical models. In the present article, we have chosen three different EAPs, PVDF (β-phase), P(VDF-TrFE), and Nylon 11, and incorporated them with different vol% (10–40 vol%) of lead-free ferroelectric ceramic filler BCZT. Here, BCZT is chosen as the filler due to its interesting properties, such as good energy storage density, high dielectric constant with low loss, and high piezoelectric properties equivalent to lead-based piezoceramics (PZT) [8]. In the present work, the specific combination of the composites chosen have practical applications. It is important to predict the properties of the polymer-piezoceramics using theoretical models to know the best performing polymer-ceramic combination and filler concentration. To predict the effective dielectric constant of the piezoceramic-polymer composites, various theoretical models such as the Maxwell and Garnett model, Furukawa, Rayleigh, Bhimasankaram-Suryanarayana-Prasad models, and Logarithmic mixture rule are used. These models suggest that the dielectric constant of the polymer/filler composite is dependent not only on the dielectric constant of the polymer and the filler, its size, shape and the volume fraction, but also on the dielectric constant of the interfacial region and the volume of the interphase region. To the best of my knowledge, no reports are available in the literature on study of dielectric properties of lead-free piezoceramic (BCZT)- various polymer composites using theoretical models. Results obtained from these models are discussed in detail. Study indicates the effectiveness of the theoretical models in predicting the polymer composite properties and help in designing the best performing composites for non-linear optics (NLO), energy storage, and energy harvesting applications, piezo catalysis and as flexible triboelectric harvesters [9 - 17].

2. Computational methods

To understand and explain the observed effective dielectric constant of the polymer composites filled with ceramic particles, different dielectric models have been formulated. Various models reported in the literature are used to predict the effective dielectric constants of the different polymer composites and rationalize their dielectric properties [3, 7]. The effective dielectric constant of the composites depends on the dielectric constant of the polymer and filler. Further, filler size, filler shape, volume fraction, and interface region between polymer and filler influence the properties [3, 7]. Therefore, different models that take the aforementioned factors into account are used to investigate the dielectric constant of the PVDF: BCZT, P(VDF-TrFE): BCZT, and Nylon11: BCZT composites. Different models are as follows:

1. Maxwell and Garnett (MG) model: The MG model gives the dielectric constant (ε_r) of the polymer composite comprising randomly dispersed spherical particles associated with a relatively high dielectric constant [7]. The effective dielectric constant of the composite is

$$\varepsilon_r = \varepsilon_1 \left(1 + \frac{3q[(\varepsilon_2-\varepsilon_1)/(\varepsilon_2+2\varepsilon_1)]}{1-q[(\varepsilon_2-\varepsilon_1)/(\varepsilon_2+2\varepsilon_1)]}\right) \quad (1)$$

where ε_1 is the dielectric constant of the polymer (dielectric constant of PVDF, P(VDF-TrFE), and Nylon 11 is 13.26, 15, and 4.25 at 10 kHz) [7, 19, 20], ε_2 is the dielectric constant of the BCZT ceramic filler (ε_2 = 2740 at 10 kHz) [21], and q is the volume fraction of the filler (varied from 10-40 vol%).

2. Furukawa Model: This model assumes a spherical shape of the filler crystallites dispersed uniformly in the polymer matrix. In this case, the dielectric constant of the composite primarily depends on the dielectric constant of the matrix [3, 7, 18]. The effective dielectric constant of the composite according to this model is given by

$$\varepsilon_r = \frac{1+2q}{1-q}\,\varepsilon_1 \quad (2)$$

where ε_1 is the dielectric constant of the polymer matrix and q is the volume fraction of the spherical crystallites.

3. Rayleigh model: The Rayleigh model is developed based on the MG and Furukawa's models for composites containing minor spherical fillers [7, 18], and the resultant effective dielectric constant (ε_r) is as follows:

$$\varepsilon_r = \frac{2\varepsilon_1+\varepsilon_2-2q(\varepsilon_1-\varepsilon_2)}{2\varepsilon_1+\varepsilon_2+q(\varepsilon_1-\varepsilon_2)}\,\varepsilon_1 \quad (3)$$

4. Bhimasankaram-Suryanarayana-Prasad (BSP) model: This model accounts for the local electric field variations and their interaction with the applied electric field plays a crucial role in determining the effective dielectric constant of the composites. The BSP model is particularly good in the case of polymer composites with a large proportion of piezoelectric crystallites [3, 7]. From the BSP model, the effective dielectric constant of the composites is shown below in Eq.4.

$$\varepsilon_r \frac{\varepsilon_1(1-q)+\varepsilon_2 q\left[\frac{3\varepsilon_1}{(\varepsilon_2+2\varepsilon_1)}\right]\left[1+\frac{3q(\varepsilon_2-\varepsilon_1)}{(\varepsilon_2+2\varepsilon_1)}\right]}{(1-q)+q\left[\frac{3\varepsilon_1}{(\varepsilon_2+2\varepsilon_1)}\right]\left[1+\frac{3q(\varepsilon_2-\varepsilon_1)}{(\varepsilon_2+2\varepsilon_1)}\right]} \quad (4)$$

5. Logarithmic mixture rule: In addition, the logarithmic simple mixture rule is also used to predict the dielectric constant of the composites as given in Eq. (5) [3,7]

$$log\ \varepsilon_r = \delta_1\ log\ \varepsilon_1 + \delta_2\ log\ \varepsilon_2 \quad (5)$$

where δ_1 and δ_2 are the volume fractions of polymer and piezoceramic fillers, respectively, and ε_1 and ε_2 are the dielectric constants of the polymer and piezoceramic filler, respectively.

3. Results and discussion

The piezoceramic filler used in this study is BCZT, which is a lead-free piezoceramic possessing properties close to lead-based piezoceramic, PZT (ε_r= 1800, tanδ = 0.02, d_{33} = 223 pC/N, Strain: 0.1–0.2 %) [4, 5]. Different polymer matrices (PVDF, P(VDF-TrFE) and Nylon11) are chosen, and various models discussed above (Eq. (1)–(5)) are applied to obtain the dielectric constants of the composites. Calculation results are summarized in Tables 1-3 for the three composites, respectively.

Estimated effective dielectric constants of PVDF: BCZT, P(VDF-TrFE): BCZT, and Nylon11: BCZT composites with varying volume fractions of BCZT from 10–40 vol% are shown in Figs. 1(a)–(c), respectively. It is observed that the dielectric constant increases with the increase of the volume fraction of ceramic filler (BCZT) in all three polymer matrices. However, different effective dielectric constant values of the composites with different models can be noted. In the case of PVDF:BCZT composites, the effective dielectric constant varied from 20 to 80 as the volume fraction increased (Fig. 1(a)). Whereas, for PVDF-TrFE: BCZT and Nylon11: BCZT composites, the effective dielectric constant lies between 20 to 130 and 5 to 60, respectively (Fig. 1(b) & (c)). The observed changes are attributed to the polymer matrix dielectric properties. Moreover, the dielectric constant significantly enhanced at 20 vol% and above of the filler content as obtained using BSP and the logarithmic mixture rule. As the piezoceramic content increases in the polymer matrices, the density of the composite increases as well as many polymer and ceramic interfaces are introduced. This leads to the enhancement in the dielectric constant due to the increased contribution of polarization resulting from the particles as well as interface polarization [3, 7, 18]. Our present computational study suggests that PVDF-TrFE: BCZT composites showed higher dielectric properties than the other two systems studied here, which showed a dielectric constant of 120 at 40 vol%. One can choose the particular composite to design flexible energy storage devices.

Table 1. Dielectric constant values at different vol% calculated using various models for PVDF–BCZT composites

Volume fractions of BCZT filler	Volume % of BCZT filler	Maxwell and Garnett model	Furukawa model	Rayleigh model	BSP model	Logarithmic mixture rule
		Effective Dielectric Constant (ε_r)				
0	0	13.3	13.3	13.3	13.3	13.3
0.1	10	17.7	17.7	17.7	18.9	22.5
0.2	20	23.2	23.2	23.0	28.9	38.5
0.3	30	30.3	30.3	29.9	45.1	46.5
0.4	40	39.8	39.8	39.2	70.6	77.5

Table 2. Dielectric constant values at different vol% calculated using various models for P(VDF-TrFE):BCZT composites

Volume fractions of BCZT filler	Volume % of BCZT filler	Maxwell and Garnett model	Furukawa model	Rayleigh model	BSP model	Logarithmic mixture rule
		Effective Dielectric Constant (ε_r)				
0	0	15.0	15.0	15.0	15.0	15.0
0.1	10	19.9	19.9	19.8	21.4	25.2
0.2	20	26.2	26.2	26.	32.7	42.5
0.3	30	34.3	34.3	33.8	50.9	71.5
0.4	40	45	45	44.2	79.7	120.4

Table 3. Dielectric constant values at different vol% calculated using various models for Nylon 11: BCZT composites

Volume fractions of BCZT filler	Volume % of BCZT filler	Maxwell and Garnett model	Furukawa model	Rayleigh model	BSP model	Logarithmic mixture rule
		Effective Dielectric Constant (ε_r)				
0	0	4.3	4.3	4.3	4.3	4.3
0.1	10	5.7	5.7	5.7	6.1	8.1
0.2	20	7.4	7.4	7.4	9.3	15.5
0.3	30	9.7	9.7	9.7	14.6	29.6
0.4	40	12.7	12.7	12.7	22.8	56.5

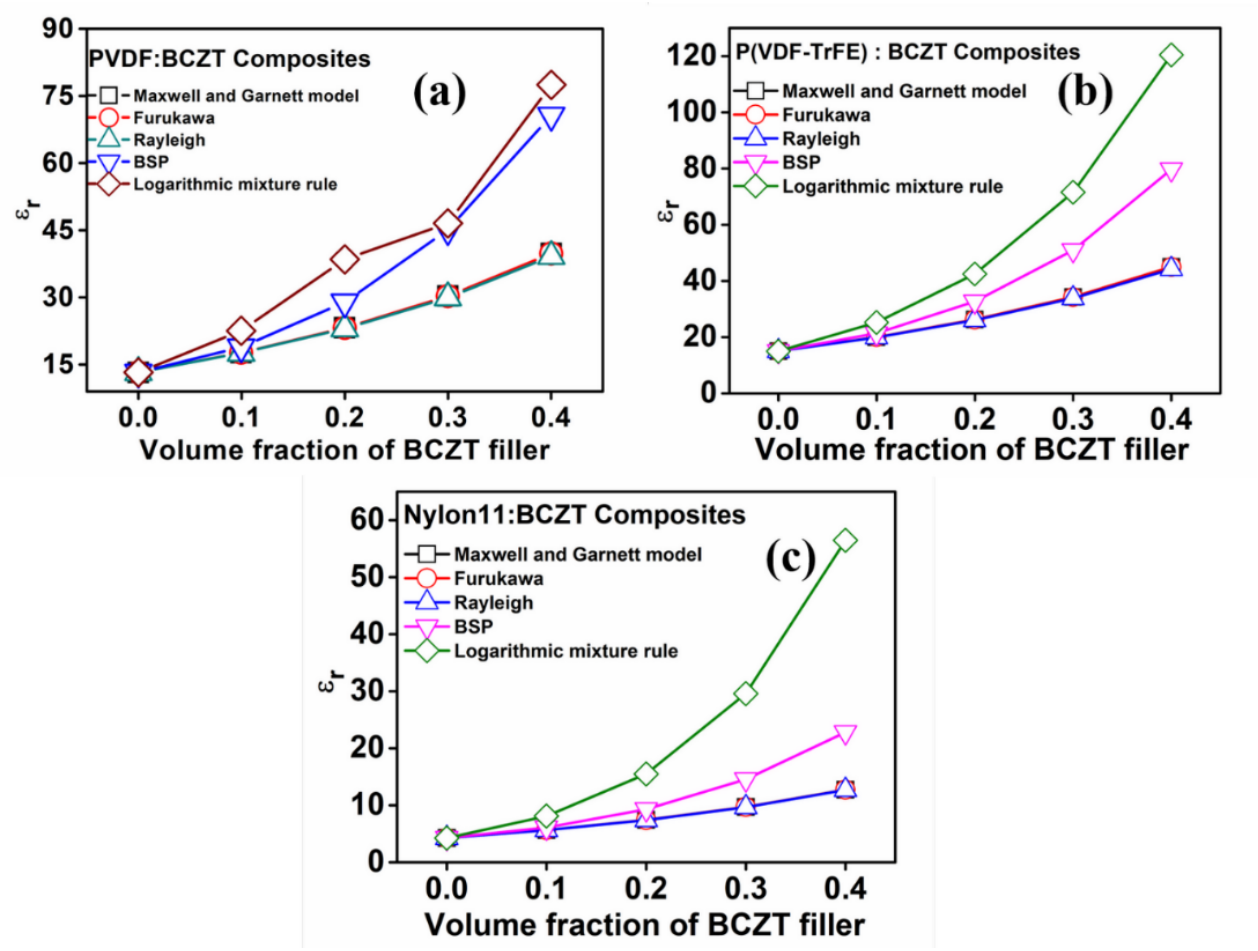

Fig. 1. Variation of the dielectric constant (ε_r) predicted by various models at a frequency of 10 kHz with different vol% of BCZT filler content, (a) PVDF:BCZT, (b) P(VDF-TrFE):BCZT, and (c) Nylon 11: BCZT composites (colour online)

4. Conclusions

The effective dielectric constant of the piezoceramic-polymer composites (PVDF: BCZT, P(VDF-TrFE): BCZT, and Nylon11: BCZT) using theoretical models is presented. The effect of the volume fraction of the filler and filler dielectric constant on the effective dielectric constant of the polymer composites is studied. The dielectric constant of the electroactive polymer-piezoceramic composites showed increasing values with the increase of BCZT filler content. The increase in dielectric constant at higher vol% has been attributed to the high density of the polymer composites and interfacial polarization between BCZT particles as well as polarizations between filler and the polymer matrix. Among the different electroactive polymers with BCZT content, P(VDF-TrFE): BCZT composites showed a higher dielectric constant value of around 120 at 40 vol%. The present study helps to understand the piezoceramic polymer composites and to predict their effective dielectric

constant to design appropriate polymer composites for non-linear optical and flexible energy storage and harvesting applications.

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