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Concentration dependent dielectric properties of Barium Titanate/Polyvenylidene Fluoride (PVDF) and $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$/Poly(VDF-TrFE) composite

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Abstract. The present study addresses the problem of quantitative prediction of effective complex relative permittivity of Barium Titanate/Polyvenylidene Fluoride (PVDF) and $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$/Poly(VDF-TrFE) biphasic ceramic-polymer composites. Theoretical results for effective relative permittivity derived from several dielectric mixture equations were fitted to the experimental data taken from the works of Prasad *et al.* (2010), Wang *et al.* (2004), Takenaka *et al.* (1991) and Yamada *et al.* (1982). The study revealed that out of the different test equations, only a few equations like modified Rother-Lichtenecker equation, Dias-Dasgupta equation or Rao equation for the real part and Bruggeman equation for the imaginary part of complex permittivity well fitted the corresponding experimental results. In the present study, some of the equations were used in their original forms, while some others were modified by choosing suitable shape-dependent parameters in order to get reasonably good agreement with experimental results. Besides, the experimental results have been proposed in the form of a mathematical model using first order exponential growth, which provided excellent fits.

Keywords: ceramic-polymer composite; permittivity; dielectric loss; model fitting

1. Introduction

Ceramic-polymer composites form a relatively new class of technologically important functional materials which combines the superior properties like hardness and stiffness of ceramics and elasticity, flexibility, low density and high breakdown strength of polymers. Consequently, ceramic-polymer composites are being increasingly utilized for their specific dielectric, ferroelectric, piezoelectric, pyroelectric, electro-optic as well as superconducting properties in microelectronic devices (Goel 2004). Piezoelectric ceramics have, in general, large dielectric constant, high piezoelectric charge coefficient as well as acoustic impedance whereas polymers have generally low dielectric constant and acoustic impedance close to those of water and human body tissue. This low value of acoustic impedance combined with higher values of piezoelectric voltage coefficients for piezoelectric polymers makes them suitable candidates for mixing with piezoelectric ceramics in order to have good strain-monitoring and hydrostatic sonar sensors (Cui 1997). Further, these

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*Corresponding author, Ph.D., E-mail: k.prasad65@gmail.com ceramic-polymer composite materials have been suggested to be viable alternative tools in piezoelectric and pyroelectric transducer applications (Das and Das-Gupta 1996).

Some of the ceramic-polymer composites are much lighter and they exhibit as much as hundred times the piezoelectric strain coefficients in comparison to those of electro-active ceramics. Ceramic nanoparticles dispersed in the ferroelectric polymer matrix are known to show much higher electromechanical coupling coefficients and higher critical temperatures. In short, these systems form the current area of research and have received intensive global attention (Xie *et al.* 2005, Kutnjak *et al.* 2005, Lam *et al.* 2005, Jha and Prasad 2010) because these composites can be prepared with excellent dielectric and mechanical properties at low temperature conditions and can be designed according to specific requirements by adjusting the relative fraction of the starting materials. However, the properties of composites depend on the connectivity of different phases (Newnham *et al.* 1980, Newnham *et al.* 1978, Smay *et al.* 2002) and their improved processability by their incorporation into devices is being investigated in the recent past to find that most of these composites show an increase of dielectric constants with the increase of volume fraction of the ceramic fillers. When the high permittivity ceramic is minor and forms a dispersed phase in a ceramic-polymer composite, the major contribution to the dielectric response comes from the continuous matrix instead of the minor ceramic phase (Kuo *et al.* 2004). Earlier, the thermoplastic polymers such as PVDF and Poly (VDF-TrFE) co-polymers had been widely used as the matrices of ceramic-polymer composites for their better dielectric and pyroelectric performances (Lam *et al.* 2003, Wang *et al.* 2004, Dang *et al.* 2005).

One of the problems inherent in composite systems has been to predict their macroscopic properties using the properties of the constituents. Many theoretical investigations on binary systems have been performed in regard to the dielectric constant, piezoelectric constant, and the elastic constant in most of which similar characteristics for continuous medium and the dispersoid have been assumed (Furukawa *et al.* 1979, Shrout *et al.* 1980, Newnham *et al.* 1980, Levassort *et al.* 2000, Prasad and Prasad 2007, Ahmad *et al.* 2009). Further, in recent years, several lead-free piezoelectric ceramic systems such as $BaTiO_3$, $(Bi_{0.5}Na_{0.5})TiO_3$, $(Na,K)NbO_3$, etc. have been studied. Among these, $(1\text{-}x)(Bi_{0.5}Na_{0.5})TiO_3–xBaTiO_3$ system has been found to be a promising lead-free piezoelectric material. A rhombohedral (F_α) – tetragonal (F_β) morphotropic phase boundary (MPB) exists at x = 0.06-0.07, where the system shows outstanding dielectric and piezoelectric properties (Wang *et al.* 2004, Takenaka *et al.* 1991). Accordingly, in the present work, a theoretical investigation on filler-dependent variation of effective relative permittivity and dielectric loss factor of $BaTiO_3$-Polyvenylidene fluoride (abbreviated hereafter BT/PVDF) and morphotropic phase boundary composition of $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$-Poly(VDF-TrFE) {abbreviated hereafter BNBT/Poly(VDF-TrFE)} binary systems with a small volume fractions of the ceramic fillers. Furthermore, the experimental results have been proposed in the form of a mathematical model using first order exponential growth, which provided excellent fits.

2. Materials and methods

Polycrystalline $BaTiO_3$ powder was prepared from AR grade (99.9%+ pure, Merck) chemicals ($BaCO_3$ and TiO_2) using standard solid-state synthesis route in air atmosphere at 1200°C for 5 h. The completion of reaction and the formation of desired compound were checked by X-ray diffraction technique. Now, 0–3 type of $(1\text{-}x)PVDF\text{-}xBaTiO_3$ composites with x = 0.10, 0.20, 0.30

were prepared by melt-mixing in a conical twin-screw extruder (Micro 5, DSM Research, Netherlands) at 260°C for 5 minutes under 150 rpm. All the samples were vacuum dried overnight at 80°C. Compression moulded films of 0.5 mm thickness were used for dielectric measurements.

As reported in the literature (Wang *et al.* 2004), $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ (BNBT) ceramic was prepared by the conventional mixed oxide high temperature solid state reaction technique at 800°C for 2 h. The ceramic powder was made by grinding and milling to reduce the particle size. The formation of single phase compound was checked by X-ray diffraction technique. Thereafter, Poly(VDF-TrFE) 70/30 mol% copolymer (Piezotech, France) was allowed to dissolve in methyl-ethyl-ketone (MEK) and the required amount of the powder in correct proportion was blended into the copolymer solution and was thoroughly agitated using a hot plate magnetic stirrer and ultrasonic agitator to evenly disperse the ceramic powder. After evaporation of the solvent at about 60°C, the dried mixture was put in an oven at 120°C for 2 h to remove the solvent completely. The composites were then compression-moulded into disk samples having a diameter of about 0.3-0.6 mm and were then slowly cooled to the room temperature. The dispersion of BNBT powder in the polymer matrix was determined from the morphology of fractured surfaces of BNBT/Poly(VDF-TrFE) composites using SEM (JEOL JSM5800LV). Silver electrodes were deposited on both the surfaces of all the fabricated composites for dielectric measurements. Real and imaginary parts of the dielectric constant data of all the composites were obtained using computer-controlled impedance analyzer.

3. Theoretical background

3.1 Real part of relative permittivity

The precise prediction of effective relative permittivity of a composite material is very important for the design of packaging materials and substrates. Several quantitative laws and simulation techniques for the prediction of effective relative permittivity have been proposed in different literatures including that mentioned above (Yamada *et al.* 1982), in which only one equation in the form of modified Effective Medium Theory Equation (MEMTE) for 0-3 composites has been used for comparison with experimental results by deriving a suitable value of shape dependent parameter for ellipsoidal particles of inclusion. On that basis, it is concluded that the theoretical values derived from the equation well-fitted the experimental results for effective permittivity of PZT/PVDF composite. In another work on $BaTiO_3$–thermosetting epoxy resin composite, it was shown that Lichtenecker mixing rule or the logarithmic rule of mixing for random media provided the best fitting prediction of effective relative permittivity (Popielarz *et al.* 2001). The universal applicability of Yamada model (Yamada *et al.* 1982) for such composites is thus at a stake. In a bid to obtain the more acceptable equation(s) for the given test composites, a number of equations as obtained through a literature survey were chosen for the study. The different test equations along with a brief introduction to the shapes and sizes of the particles or the suitable empirical values of the shape dependent parameters involved in them are given below.

(a) Knott equation (Knott 1993)

$$\varepsilon_{eff} = \frac{\varepsilon_2[1-\{(\varepsilon_2-\varepsilon_1)(1-f)\}]}{\varepsilon_1+(\varepsilon_2-\varepsilon_1)(1-f)^{1/3}} \tag{1}$$

with f is the volume fraction of the inclusion material. Here ε_1 and ε_2 represent the relative permittivity of the host and inclusion particles, respectively, and ε_{eff} is the effective relative permittivity of the mixture. The same terminology has been used in all subsequent equations except where indicated otherwise. In the paper containing the above Eq. (1) a sample 3D cubic lattice and spherical particles have been chosen for the analysis.

(b) Rother-Lichtenecker equation (RLE) or Cuming equation (Brookner 1988)

$$\varepsilon_{eff} = \exp\left(\sum f_i \ln \varepsilon_i\right) \tag{2}$$

where ε_i is the relative permittivity of the i^{th} component of the mixture and f_i is the volume fraction of the component.

(c) Modified Rother-Lichtenecker equation (MRLE with $k = 0.7$) (Rao *et al.* 2000)

$$\varepsilon_{eff} = \exp[\ln \varepsilon_1 + f_2(1-k)\ln(\varepsilon_2/\varepsilon_1)] \tag{3}$$

Eqs. (2) and (3) are nothing but general representations of logarithmic law of mixing for a chaotic or statistical mixture. The Eq. (2) does not contain a shape-dependent parameter whereas Eq. (3) contains it in the form of k.

(d) Webmann equation (Webman *et al.* 1977) or Furukawa equation (FE) or equation from Effective Medium Theory (EMTE) (Furukawa 1989)

$$\varepsilon_{eff} = \varepsilon_B \frac{1 + 2f_A\{(\varepsilon_A - \varepsilon_B)/(\varepsilon_A + 2\varepsilon_B)\}}{1 - f_A\{(\varepsilon_A - \varepsilon_B)/(\varepsilon_A + 2\varepsilon_B)\}} \tag{4a}$$

for the binary system AB in small concentration C_A of the component A. Here A has been taken as the inclusion and B the host, in contrast with other chosen equations. In order to maintain uniformity of notations in all the test equations, A and B subscripts are to be interchanged to get an equation in final form, based on Hashin-Shtrikman composite cylinder model (Hashin and Shtrikman 1963) as

$$\varepsilon_{eff} = \frac{\varepsilon_1[(1+2f)\varepsilon_2 + 2\varepsilon_1(1-f)]}{\varepsilon_2(1-f) + (2+f)\varepsilon_1} \tag{4b}$$

The above equation was derived with the consideration of medium to be random with the cells embedded in a medium assumed to be homogeneous on scales smaller than the correlation length, but inhomogeneous on scales smaller than it, having its permittivity ε_1. The cells were assumed to be spherical in shape, having dimensions of their correlation length $\sim b$ for each of them centered on the points $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ .... $\boldsymbol{r}_N$ having a constant value of dielectric constant ε_2 in each cell. The correlation length or particle diameters were assumed to be smaller than the wavelength of the electromagnetic waves used.

(e) Maxwell-Wagner equation (Hashin and Shtrikman 1963)

$$\varepsilon_{eff} = \varepsilon_1 \frac{\varepsilon_2 + 2\varepsilon_1 + 2f(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2 + 2\varepsilon_1 - f(\varepsilon_2 - \varepsilon_1)} \tag{5}$$

The above Eq. (5) was derived almost on the same considerations of hard spherical particles embedded in the host medium as solutes in dilute suspensions.

(f) Skipetrov equation (Skipetrov 1999)

$$\varepsilon_{eff} = \varepsilon_1 \frac{1 + \{3f(\varepsilon_2 - \varepsilon_1)\}}{\varepsilon_1(2+f) + \varepsilon_2(1-f)} \tag{6}$$

This equation is perhaps the first non-perturbative equation which is original and more transparent than others and is assumed to give more correct results under tough situations i.e., with high contrast $\varepsilon_2/\varepsilon_1$ and large volume fraction (f), also applicable to the systems with fluctuating dielectric function. In one of our previous studies (Ahmad *et al.* 2009), it was found that all the three Eqs. (4)-(6) produced almost identical results at least for five test materials and hence in that paper their common results were shown under the common name Maxwell-Wagner-Webmann-Skipetrov equation (MWWSE).

(g) Modified Cule-Torquato equation (MCTE) (Prasad and Prasad 2007)

$$\varepsilon_{eff} = \frac{\varepsilon_1(1+2a^2\beta)}{b^2 - a^2\beta} \tag{7}$$

with $\beta = (\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + \varepsilon_1)$, a = radius of the cylindrical core having permittivity ε_1, b = radius of the surrounding concentric shells having permittivity ε_2, and f = volume fraction of the inclusion material = $(a/b)^2$.

(h) Taylor's equation for random angular distribution of needles (Al-Jishi and Taylor 1985)

$$3\varepsilon_r(\varepsilon_r - \varepsilon_H) = f(\varepsilon_I - \varepsilon_H)(2\varepsilon_I + \varepsilon_r) \tag{8a}$$

where ε_r represents the effective relative permittivity of mixture and the subscripts I and H represent the inclusion and host, respectively. Thus, $\varepsilon_H \equiv \varepsilon_1$ and $\varepsilon_I \equiv \varepsilon_2$. After rearranging the terms, one gets

$$\varepsilon_{eff} = \frac{1}{6}[\{3\varepsilon_1 + f(\varepsilon_2 - \varepsilon_1)\} \pm \sqrt{\{3\varepsilon_1 + f(\varepsilon_2 - \varepsilon_1)\}^2 + 24f\varepsilon_2(\varepsilon_2 - \varepsilon_1)}] \tag{8b}$$

(i) Taylor's equation for random angular distribution of disks (Al-Jishi and Taylor 1985)

$$3(\varepsilon_r - \varepsilon_H)(\varepsilon_I + \varepsilon_r) = \mathrm{f}(\varepsilon_I - \varepsilon_H)(5\varepsilon_r + \varepsilon_I) \tag{9a}$$

which finally gives

$$\varepsilon_r = \varepsilon_{eff} = \frac{1}{6}[\{(5f-3)(\varepsilon_2 - \varepsilon_1)\} \pm \sqrt{\{(3-5f)(\varepsilon_2 - \varepsilon_1)\}^2 + 12\varepsilon_2\{f(\varepsilon_2 - \varepsilon_1) + 3\varepsilon_1\}}] \tag{9b}$$

(j) Lewin's equation (LE) (Al-Jishi and Taylor 1985)

$$\varepsilon_{eff} = \frac{3f(\varepsilon_2 - \varepsilon_1)}{\{\varepsilon_1(1+2f) + \varepsilon_2(1-f)\}} + 1 \tag{10}$$

(k) Sillar's equation (Dionne *et al.* 1976)

$$\varepsilon_{eff} = \frac{\varepsilon_1[\varepsilon_1 + D(1-f) + f(\varepsilon_2 - \varepsilon_1)]}{\varepsilon_1 + D(1-f)(\varepsilon_2 - \varepsilon_1)} \tag{11}$$

where D = depolarization parameter, depending on the shape of particles.

(l) Wiener equation (WE) (Wiener 1912, Prasad *et al.* 2001)

$$\frac{\varepsilon_r - 1}{\varepsilon_r + u} = \frac{f(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2 + u} + \frac{(1-f)(\varepsilon_1 - 1)}{\varepsilon_1 + u} \tag{12a}$$

which finally gives

$$\varepsilon_r = \varepsilon_{eff} = \frac{1}{2}\left[\left\{\left(\frac{f(\varepsilon_2-1)(\varepsilon_1+u)+(1-f)(\varepsilon_1-1)(\varepsilon_2+u)}{(\varepsilon_2+u)(\varepsilon_1+u)}\right)(u+1)\right\}-(u+1)\right] \tag{12b}$$

where u = form number depending on the shape of the particles.

(m) Bruggeman equation or modified EMT equation or Dias-Dasgupta equation using Takashi-Yamada model (Yamada *et al.* 1982, Das and Das-Gupta 1994) or Rao equation (Rao *et al.* 2000) commonly designated as MEMTE

$$\varepsilon_{eff} = \varepsilon_B\left[1+\frac{f_A(\varepsilon_A-\varepsilon_B)}{\varepsilon_B+n(1-f_A)(\varepsilon_A-\varepsilon_B)}\right] \tag{13a}$$

where n is the shape-dependent parameter taken to be equal to 0.1 in the present work.

$$\varepsilon_{eff} = \varepsilon_1\left[1+\frac{f(\varepsilon_2-\varepsilon_1)}{\varepsilon_1+n(1-f)(\varepsilon_2-\varepsilon_1)}\right] \tag{13b}$$

In the given model, the particles were assumed to be ellipsoidal in shape dispersed in a continuous medium.

(n) Jayasundere-Smith equation (J-SE) (Jayasundere and Smith 1993, Jayasundere *et al.* 1994, Kuo *et al.* 2004)

$$\varepsilon_{eff} = \frac{[\{\varepsilon_1 f_1+\varepsilon_2 f_2(3\varepsilon_1/(\varepsilon_2+2\varepsilon_1))\}\{1+3f_2(\varepsilon_2-\varepsilon_1)/(\varepsilon_2+2\varepsilon_1)\}]}{[\{f_1+f_2(3\varepsilon_1/(\varepsilon_2+2\varepsilon_1))\}\{1+3f_2(\varepsilon_2-\varepsilon_1)/(\varepsilon_2+2\varepsilon_1)\}]} \tag{14}$$

with $f_1 + f_2 = 1$, as before. Jayasundere-Smith has presented the above expression by modifying the well-known Kerner expression (Kerner 1956) for the dielectric constant of a binary dielectric in 0–3 composite with large volume fraction of the dielectric filler. The 0–3 composite is composed of piezoelectric spherical particles under the condition $\varepsilon_2 >> \varepsilon_1$, taking into consideration the interactions between neighboring spheres. The limitations to the applicability of Jayasundere equation is mentioned in the literature (Jayasundere and Smith 1993) that its application needs the size effect on the difference in dielectric constant of ceramics in the form of un-sintered powder and sintered bulk to be considered.

(o) Poon-Shin equation (P-SE) (Poon and Shin 2004)

$$\varepsilon_{eff} = \varepsilon_m\left[1+\frac{f\{(\varepsilon_i/\varepsilon_m)-1\}}{[f+(1+f/3)\{(\varepsilon_i/\varepsilon_m)(1-f)+f+2\}]}\right] \tag{15}$$

where ε_m = permittivity of matrix (host)≡ ε_1, ε_m = permittivity of inclusion material≡ ε_2, f = volume fraction of inclusion materials, as before and ε_{eff} = effective permittivity of binary composite.

3.2 Imaginary part of relative permittivity

The equations governing the filler-concentration dependent variation of effective dielectric loss factor of composites, unlike those for dielectric constant, are fewer in number. However, an equation given by Bruggeman (Bruggeman 1935, Wang *et al.* 2004) reads as follows

$$\varepsilon''_{eff} = \varepsilon'' = \frac{\varepsilon''_p[(\varepsilon_c'-\varepsilon')(\varepsilon_c'+2\varepsilon_p')\varepsilon']}{[(\varepsilon_c'-\varepsilon_p')(\varepsilon_c'+2\varepsilon')\varepsilon_p']}+\varepsilon_c''\frac{3(\varepsilon'-\varepsilon_p')\varepsilon'}{(\varepsilon_c'-\varepsilon_p')(\varepsilon_c'+2\varepsilon')} \tag{16}$$

where the subscripts c and p represent ceramic and polymer respectively, and the quantity without a subscript refers to the composite. A single prime over ‘epsilon’ corresponds to relative permittivity while double prime corresponds to dielectric loss factor. In the course of literature survey, no other such equations were found for study. However, the above sole equation (Eq. (16)) paved the way for using all the other preceding fifteen equations for effective relative permittivity ($=\varepsilon'$) to be put in Eq. (16) to get the corresponding fifteen values of dielectric loss factor ($=\varepsilon''$) for their comparison with experimental results for effective loss factor of the composite to get the best fitting prediction equation(s).

4. Results and discussion

Figs. 1 and 2, respectively, show the filler concentration dependent variation of experimental as well as theoretically predicted acceptable results for effective relative permittivity and dielectric loss factor of BT/PVDF ceramic-polymer composites. The percentage difference between theoretically predicted and experimentally observed results of the same composite as a function of volume fraction of BT in the composite are shown in the inset of Figs. 1 and 2. Comparison of theoretically derived results for filler concentration dependent variation of effective relative permittivity of BT/PVDF ceramic-polymer composite with experimental results showed that out of at least thirteen independent test equations, only the unmodified Rother-Lichtenecker equation (RLE) and Modified Rother-Lichtenecker equation (MRLE with k = 0.7) proven themselves to be treated as acceptable. As far as the filler concentration dependent variation of dielectric loss factor of the BT/PVDF composite is concerned, it was observed that RLE, J-SE, WE, P-SE and MEMTE (n = 0.1) did not show their acceptability for this variation. On the other hand, almost all the other test equations namely, MRLE (k = 0.7), EMTE, LE and MCTE showed tolerably good acceptability.

The detailed analytical study revealed that out of the so-called more acceptable dielectric mixture equations for random media, as evidenced by their plots, only a few showed tolerably small percentage errors as compared with their corresponding experimental values. Figs. 1 and 2,

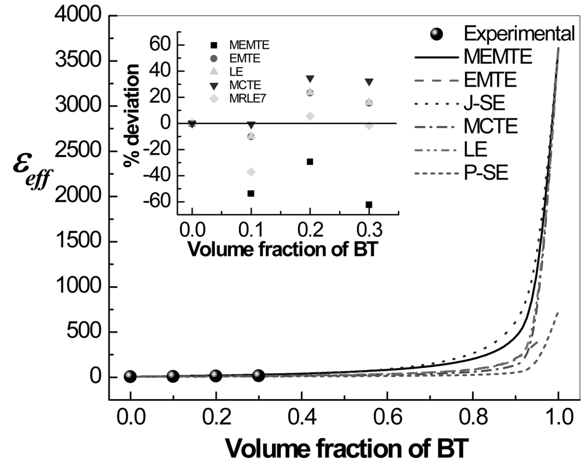

Fig. 1 Variation of effective relative permittivity of BT/PVDF 0-3 composite as a function of volume fraction of BT in the composite. Inset: Variation of percentage difference in experimental and theoretically predicted values of effective relative permittivity of BT/PVDF 0-3 composite samples as a function of volume fraction of BT in the composite

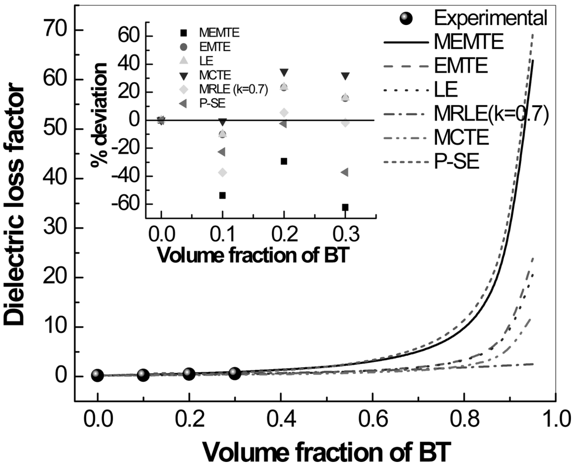

Fig. 2 Variation of effective dielectric loss factor of BT/PVDF 0-3 composite as a function of volume fraction of BT in the composite. Inset: Variation of percentage difference in experimental and theoretically predicted values of effective dielectric loss factor of BT/PVDF 0-3 composite samples as a function of volume fraction of BT in the composite

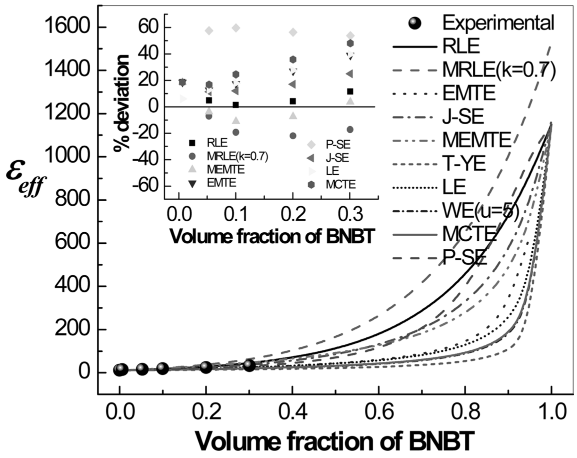

Fig. 3 Variation of effective relative permittivity of BNBT/Poly(VDF-TrFE) 0-3 composite as a function of volume fraction of BNBT in the composite. Inset: Variation of percentage difference in experimental and theoretically predicted values of effective relative permittivity of BNBT/Poly(VDF-TrFE) 0-3 composite samples as a function of volume fraction of BNBT in the composite

respectively, indicated that only MEMTE (n = 0.1) provided errors ≈1.11% to 4.28% and P-SE provided errors ≈10.65% to 38.13%, while other equations including RLE or MRLE (k = 0.7) provided errors ≈80% to 620%, respectively. These results indicated that MEMTE (n = 0.1) and P-SE for predicting the filler concentration dependent variation of effective relative permittivity of BT/PVDF composite samples producing minimal percentage as compared with corresponding experimental values may be retained in their original forms. As regards the variation of dielectric loss factor of BT/PVDF composite as a function of BT in it, it was seen that neither of the predicting equations like LE, MCTE, MRLE (k = 0.7) and P-SE [all applied to Bruggeman equation (Eq. (16))]

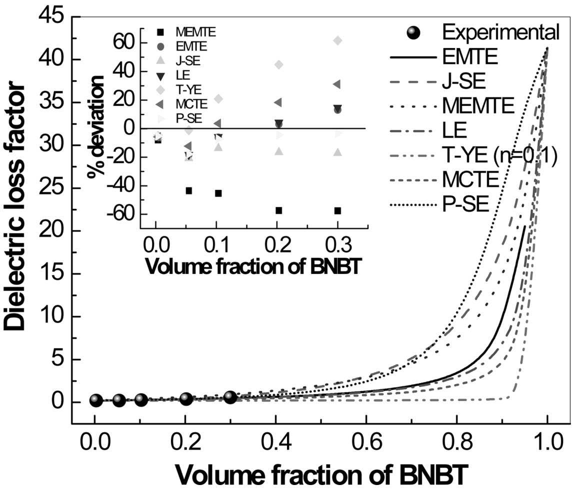

Fig. 4 Variation of effective dielectric loss factor of BNBT/Poly(VDF-TrFE) 0-3 composite as a function of volume fraction of BNBT in the composite. Inset: Variation of percentage difference in experimental and theoretically predicted values of effective dielectric loss factor of BNBT/Poly(VDF-TrFE) 0-3 composite samples as a function of volume fraction of BNBT in the composite

did provide satisfactory results. For example, EMTE and LE provided errors ≈10% to 23% while P-SE provided errors ≈23.7% to 37.12%. In view of these results, these equations (EMTE, LE and P-SE applied to Bruggeman equation) may be treated as tolerably good for predictive purposes.

The filler concentration dependent variation of experimental as well as theoretically predicted acceptable results for effective relative permittivity and dielectric loss factor of the morphotropic phase boundary composition BNBT/Poly(VDF-TrFE) ceramic-polymer composites are, respectively, shown in Figs. 3 and 4 and the percentage difference between theoretically predicted and experimentally observed results of the same composite as a function of volume fraction of BNBT is shown in the inset of Figs. 3 and 4. For the filler concentration dependent variation of effective relative permittivity of BNBT/Poly(VDF-TrFE) ceramic-polymer composites it transpired that only RLE and MRLE (k = 0.7) provided the most acceptable results, while the other equations did not provide acceptable ones. Next followed the RLE, J-SE, MEMTE (n = 0.1) and EMTE while other equations did not provide acceptable results. As far as the filler concentration dependent variation of dielectric loss factor of the BNBT/Poly(VDF-TrFE) ceramic-polymer composites is concerned, it was seen that equations like RLE, MRLE and WE etc. did not provide reasonable acceptability.

As regards the filler concentration dependent variation of effective relative permittivity of BNBT/Poly(VDF-TrFE) composite shown in Fig. 3, the results revealed that only P-SE, EMTE, J-SE may be treated as acceptable in giving deviation ~(3 to 13%), (12 to 20%) and (0.36 to 17%), respectively, as compared with experimental values. On the other hand, RLE, MRLE (k = 0.7) gave errors as high as 80% and 99%, respectively. With reference to Fig. 3 (inset), it may be seen that the percentage deviation in experimental and theoretically predicted values of dielectric loss factor of BNBT/Poly(VDF-TrFE) composite in the light of EMTE, LE, J-SE, P-SE and MCTE are ~(3.09 to 18.17), (4.23 to 18.12), (6.14 to 20.70), (6.16 to 27.03) and (3.53 to 31.08), respectively, while the corresponding values for MEMTE are (8.27 to 70.0%). From the results shown in Fig. 4 (inset) it may be inferred that for the filler concentration dependent variation of the effective dielectric loss

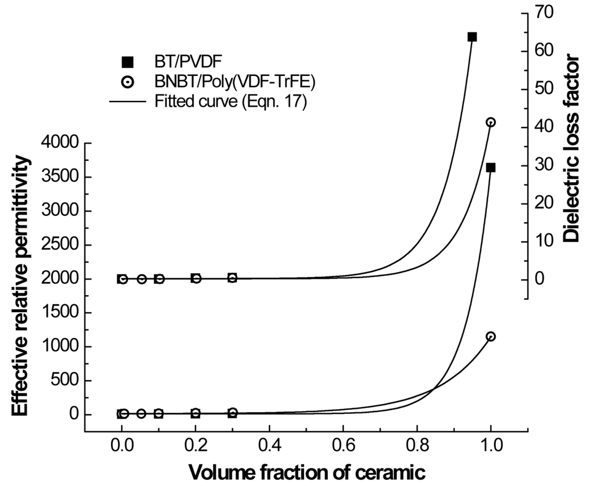

Fig. 5 Ceramic (filler) concentration dependent effective relative permittivity and dielectric loss of BT/PVDF and BNBT/Poly(VDF-TrFE) 0-3 ceramic-polymer composites at 1 kHz with theoretical fit Eq. (17)

factor of BNBT/Poly(VDF-TrFE) composite samples, almost all the test equations excepting MEMTE may be used in their original forms.

On the basis of the above analyses it transpired that mixture equations for effective complex permittivity did not agree well with the experimental results for the test ceramic-polymer composite materials for the present study. In a bid to find an acceptable solution to the problem, it was proposed to provide new model for the ceramic (filler) concentration dependent variation of complex permittivity of the test composite materials under the present study by way of curve-fitting with experimental data. In this regard the first order exponential growth type of mathematical model in the form.

$$Y = Y_0 + A\exp(x/t) = Y_o + A\exp(\beta x) \tag{17}$$

where Y_o, A and t or β $(=1/t)$ are the model parameters and x is the volume fraction of ceramic in the composite, was found to yield results as provided in Table 1 showed that the values of r^2 are approaching unity for almost all the test materials and for both material properties *viz.* real and imaginary parts of complex permittivity. In the present context, the term (Y_o+A) corresponds to the value of real part of permittivity and dielectric loss factor as per the chosen variation out of the two types (corresponding to the two material properties) at $x = 0$ i.e., for the polymer matrix, while the term $[\ Y_o + A\exp(\beta x)\ ]$ for $x = 1$ corresponds to the values of the same dielectric properties for the ceramic filler. Here β may be designated as the filler concentration dependent 'permittivity growth parameter'. Fig. 5 illustrates the ceramic (filler) concentration dependent dielectric properties of both the composites along with the fitted curve (Eq. (17)). It is observed that the experimental data fits excellently well (Fig. 5; $r^2 > 0.99$, Table 1) with the proposed theoretical model. In the present study almost the same type of ceramic fillers such as ($BaTiO_3$ and BNBT) and polymers like [PVDF and Poly(VDF-TrFE)] were chosen as test materials. Consequently, almost the same order of values of t $(=1/\beta) \approx 0.07$, with the only exception of 0.1361 in case of real part of permittivity for BNBT/Poly(VDF-TrFE) composite, were obtained for all the test materials and for both the material properties *viz.* dielectric constant and dielectric loss factor. However, from the study it transpired that if quite different types of ceramic fillers as well as polymer matrices were chosen as the test materials,

Table 1 Fitting parameters for the first order exponential growth regression equation applied to experimental data of effective relative permittivity and dielectric loss of BT/PVDF and BNBT/Poly(VDF-TrFE) 0-3 ceramic-polymer composites at 1 kHz

Equations → Parameters ↓	Exponential growth: $Y = Y_o + A\exp(x/t)$			
	Y_o	A	t	r^2
ε' , BT/PVDF	12.04277	0.00135	0.06756	0.99999
ε'' , BT/PVDF	0.37039	2.8876E-4	0.07723	0.99995
ε' , BNBT/Poly(VDF-TrFE)	16.1197	0.7305	0.1361	0.99982
ε'' , BNBT/Poly(VDF-TrFE)	0.31448	8.7970E-5	0.0766	0.99991

the filler concentration dependent ‘permittivity growth parameter (β)’ would certainly assume different values in view of the fact that at least due to the different nature of densification of the samples (lighter polymer particles being replaced by denser ceramic particles) as the ceramic concentration is increased. The growth may also be ascribed to the different ratios of the permittivities of ceramic to polymers (although always greater than 1). Thus the values of β for different test composite materials will certainly throw some light on the nature (sharp or flat) of such type of variation and could thus assume a type of calibration parameter, which may be useful for further study.

5. Conclusions

The effective complex relative permittivity of BT/PVDF and BNBT/Poly(VDF-TrFE) 0-3 ceramic-polymer biphasic composite systems as functions of broad compositional range have been investigated and the experimental results have been compared with the theoretical results derived from various predictive equations. Some of the equations governing the ceramic filler concentration dependent variation of complex permittivity of ceramic-polymer composites have been used in their original forms, while some others have been modified by choosing suitable shape-dependent parameters in the present study in order to get reasonably good agreement with experimental results. The study revealed that in most of the cases the first order exponential growth type of model provided the most acceptable fits with experimental results for effective complex permittivity of BT/PVDF and BNBT/Poly(VDF-TrFE) 0-3 ceramic-polymer biphasic composite systems and only a few well- established and well known dielectric mixture equations did provide good agreements with experimental results.

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References

Ahmad, Z., Prasad, A. and Prasad, K. (2009), “A comparative approach to predicting effective dielectric, piezoelectric and elastic properties of PZT/PVDF composites", *Phys. B: Conden. Matter*, **404**(20), 3637-3644.

Al-Jishi, R. and Taylor, P.L. (1985), "Equilibrium polarization and piezoelectric and pyroelectric coefficients in poly(vinylidene fluoride)", *J. Appl. Phys*., **57**(3), 902-906.

Brookner, E. (1988), "Aspects of modern radars", Artech House, Norwood, MA.

Bruggeman, D.A.G. (1935), "Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. DielektrizitaEtskonstanten und LeitfaEhigkeiten der MischkoErper aus isotropen Substanzen", *Ann. Phys. Lpz*., **416**(7), 636-664.

Cui, C., Baughman, R.H., lgbal, Z., Kazmar, T.R. and Dalstrom, D.K. (1997), "Improved piezoelectric ceramic/polymer composites for hydrophone applications", *Synthetic Met.*, **85**(1-3), 1391-1392.

Dang, Z.M. and Nan, C.W. (2005), "Dielectric properties of LTNO ceramics and LTNO/PVDF composites", *Ceram. Int*., **31**(2), 349-351.

Das, C.J. and Das-Gupta, D.K. (1994), "Ferroelectric polymers and ceramic-polymer composites", *Key Eng. Mater*., **92-93**, 217-248.

Das, C.J. and Das-Gupta, D.K. (1996), "Inorganic ceramic/polymer ferroelectric composite electrets", *IEEE T. Dielect El. In.*, **3**(5), 706-734.

Dionne, F.F., Firtzgerald, J.F. and Aucoin, R.C. (1976), "Dielectric constants of paraffin wax TiO_2 mixtures", *J. Appl. Phys*., **47**(4), 1708-1709.

Furukawa, T. (1989), "Piezoelectricity and pyroelectricity in polymers", *IEEE T. El. In*., **24**(3), 375-394.

Furukawa, T., Ishida, K. and Fukuda, E. (1979), "Piezoelectric properties in the composite systems of polymers and PZT ceramics", *J. Appl. Phys*., **50**(7), 4904-4913.

Goel, M. (2004), "Recent developments in electroceramics: MEMS applications for energy and environment", *Ceram. Int.*, **30**(7), 1147-1154.

Hashin, Z. and Shtrikman, S.A. (1963), "A variational approach to the theory of the elastic behaviour of multiphase materials", *J. Mech. Phys. Solids*, **11**(2), 127-140.

Jayasundere, N. and Smith, B.V. (1993), "Dielectric constant for binary piezoelectric 0-3 composites", *J. Appl. Phys*., **73**(5), 2462-2467.

Jayasundere, N., Smith, B.V. and Dunn, J.R. (1994), "Piezoelectric constant for binary piezoelectric 0-3 connectivity composites and the effect of mixed connectivity", *J. Appl. Phys*., **76**(5), 2993-2999.

Jha, A.K. and Prasad, K. (2010), "Ferroelectric $BaTiO_3$ nanoparticles: biosynthesis and characterization", *Colloid. Surface B.*, **75**(1), 330-334.

Kerner, E.H. (1956), "The electrical conductivity of composite media", *Proc. Phys. Soc*., **69**(8), 802-807.

Knott, E.F. (1993), "Dielectric constant of plastic foams", *IEEE T. Antenn. Propag*., **41**(8), 1167-1171.

Kuo, D.H., Chang, C.C., Su, T.Y., Wang W.K. and Lin, B.Y. (2004), "Dielectric properties of three ceramic/epoxy composites", *Mater. Chem. Phys.*, **85**(1), 201-206.

Kutnjak, Z., Vodopivec, B., KuöËer, D., Kosec, M., Bobnar, V. and Hilczer, B. (2005), "Calorimetric and dielectric study of vinylidene fluoride-trifluoroethylene-based composite", *J. Non-Cryst. Solids*, **351**(14-15), 1261-1265.

Lam, K.H. Wang, X. and Chan, H.L.W. (2005), "Piezoelectric and pyroelectric properties of $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$/P(VDF-TrFE) 0-3 composites", *Compos. Part A - Appl. S.*, **36**(11), 1595-1599.

Lam, K.H., Chan, H.L.W., Luo, H.S., Yin, Q.R., Yin, Z.W. and Choy, C.L. (2003), "Dielectric properties of 65PMN-35PT/P(VDF-TrFE) 0-3 composites", *Microelectron. Eng*., **66**(1-4), 792-797.

Levassort, F., Topolov, V.Y. and Lelhiecq, M. (2000), "A comparative study of different methods of evaluating effective electromechanical properties of 0-3 and 1-3 ceramic/polymer composites", *J. Phys. D Appl. Phys.*, **33**(16), 2064-2069.

Newnham, R.E, Skinner, D.P. and Cross, L.E. (1978), "Connectivity and piezoelectric-pyroelectric composites", *Mater. Res. Bull*., **13**(5), 525-536.

Newnham, R.E., Bowen, L.J., Klicker, K.A. and Cross. L.E. (1980), "Composite piezoelectric transducers", *Mater. Eng*., **2**(2), 93-106.

Newnham, R.E., Skinner, D.P., Klicker, K.A., Bhalla, A.S., Hardiman, B. and Gururaja, T.R. (1980), "Ferroelectric ceramic-plastic composites for piezoelectric and pyroelectric applications", *Ferroelectrics*, **27**(1), 49-55.

Poon, Y.M. and Shin, F.G. (2004), "A simple explicit formula for the effective dielectric constant of binary 0-3 composites", *J. Mater. Sci*., **39**(4), 1277-1281.

Popielarz, R., Chiang, C.K., Nozaki, R. and Obrzut, J. (2001), "Dielectric properties of polymer/ferroelectric ceramic composites from 100 Hz to 10 GHz", *Macromolecules*, **34**(17), 5910-5915.

Prasad, A. and Prasad, K. (2007), "Effective permittivity of random composite media: A comparative study", *Phys. B Conden. Mat.*, **396**(1-2), 132-137.

Prasad, A., Bagchi, S. and Pathak, S.C. (2001), "Empirical formulation of permittivity build-up of bound rutile samples-I", *Indian J. Pure Ap. Phy.*, **39**(6), 397-405.

Prasad, K., Prasad, A., Chandra, K.P. and Kulkarni, A.R. (2010), "Electrical conduction in 0-3 $BaTiO_3$/PVDF composites", *Int. Ferroelectrics*, **117**(1), 55-67.

Rao, Y., Qu, J. Wong, C.P. and Marinis, T. (2000), "A precise numerical prediction of effective dielectric constant for polymer-ceramic composite based on effective-medium theory", *IEEE T. Compon. Pack. T.*, **23**(4), 680-683.

Shrout, T.R., Bawen, L.J. and Schulze, W.A. (1980), "Extruded PZT/polymer composites for electromechanical transducer applications", *Mater. Res. Bull.*, **15**(10), 1371-1379.

Skipetrov, S.E. (1999), "Effective dielectric function of a random medium", *Phys. Rev. B*, **60**(18), 12705-12709.

Smay, J.E., Cesarano, J., Tuttle, B.A. and Lewis, J.A. (2002), "Piezoelectric properties in the composite systems of polymers and PZT ceramics", *J. Appl. Phys.*, **50**(7), 6119-6127.

Takenaka, T., Maruyama K.I. and Sakata, K. (1991), "$(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ system for lead-free piezoelectric ceramics", *Jpn. J. Appl. Phys.*, **30**, 2236-2239.

Taylor, L. (1965), "Dielectric properties of mixtures", *IEEE T. Antenn. Propag.*, **13**(6), 943-947.

Wang, X.X., Lam, K.H., Tang, X.G. and Chan, H.L.W. (2004), "Dielectric characteristics and polarization response of lead-free ferroelectric $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$-P(VDF-TrFE) 0-3 composites", *Solid State Commun.*, **130**(10), 695-699.

Webman, I., Jortner, J. and Cohen, M.H. (1977), "Theory of optical and microwave properties of microscopically inhomogeneous materials", *Phys. Rev. B*, **15**(12), 5712-5723.

Wiener, O. (1912), "Die Theorie des Mischkorpers fr das Feld der Stationaren Strdmung", *Abh. Math. Phys. Kl. Sachs Akad. Wiss: Leipzig*, **32**, 509-514.

Xie, S.H. Zhu, B.K., Wei, X.Z., Xu, Z.K. and Xu, Y.Y. (2005), "Polyimide/$BaTiO_3$ composites with controllable dielectric properties", *Compos. Part A - Appl. S.*, **36**(8), 1152-1157.

Yamada, T., Ueda, T. and Kitayama, T. (1982), "Piezoelectricity of a high-content lead zirconate titanate/polymer composite", *J. Appl. Phys.*, **53**(6), 4328-4333.