An Analytical Model for the Effective Dielectric Constant of a 0-3-0 Composite

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An analytical expression for prediction of the effective dielectric constant of a three phase 0-3-0 ferroelectric composite is presented. The analytical results are verified with the experimental results from Nan et al. (2002, "Three-Phase Magnetoelectric Composite of Piezoelectric Ceramics, Rare-Earth Iron Alloys, and Polymer," Appl. Phys. Lett., 81(20), p. 3831). The analytical model is extended to include the shape of a third phase inclusion to examine the influence of the shape (of the inclusion) on the effective dielectric constant of the composite. The dielectric constant increases as much as seven times when the aspect ratio of the conducting inclusion particle is increased from 1 (sphere) to 10 (spheroid). A comparison of the analytical predictions with the experimental values, which indicate that the increase in aspect ratio of the inclusions has a significant effect on the overall dielectric constant of the composite. [DOI: 10.1115/1.4004811]

Keywords: piezoelectric composite, dielectric constant, 0-3-0 composite

1 Introduction

Composite ferroelectric materials have been investigated for smart materials in applications such as structural health monitoring of civil structures [1–4] magnetoelectric sensors [5], and transducer applications [6]. Toward the development of structural health monitoring sensors, researchers have developed cement based 0-3 piezoelectric composites [2–4] because of their compatibility with materials commonly used for civil structural applications; tunable acoustic impedance that can be matched to the host structural material and piezoelectric strain coefficients that are higher than polymer based composites, e.g., 30 (10^{-12} C/N) and 9 (10^{-12} C/N) for piezoelectric-cement and polymer based composites, respectively, with equal volume fractions of piezoelectric transducer (PZT). Also, 0-3 PZT-cement composites can have higher electromechanical coupling factors (20% and 15% for a PZT-cement and polymer based composites, respectively), for smaller volume fractions of PZT, e.g., 0.7 and 0.8 for PZT-cement and polymer based composites, respectively [2–4,7–9].

In order to enhance the dielectric constant and electromechanical properties of 0-3 composites, researchers have begun to investigate three phase, 0-3-0 composites. For example, percolative three phase composites comprised of uniformly distributed conductive filler particles within a ferroelectric polymer matrix have been studied [5,10–13] because these materials demonstrate an increase in dielectric properties with an increase in the conductive filler content. Researchers have also concluded that the dielectric constant and piezoelectric strain coefficient of these materials are highly sensitive to the conductive phase content above the percolation limit and within the percolation transition. They have also concluded that having a conductive phase content above the percolation limit can result in substantial dielectric loss and leakage current. Hence, these workers have concluded that three phase materials such as these are practical for application below the percolation limit [14–16]. Here, we present an analytical model for the prediction of the effective dielectric constant of a three phase piezoelectric composite material, that is, comprised of piezoelectric, matrix and conductive materials that posses 0-3-0 connectivity. We then use this model to investigate the influence of conductive inclusion shape on the effective dielectric constant of the composite.

The term connectivity [17–19] refers to the arrangement of phases within the composite, which influences the piezoelectric composite's electromechanical properties. In general, ten connectivity patterns can be used for a diphasic system, which refers to the manner in which individual phases are self-connected. The arrangement of phases within the composite referred to as connectivity influences the electromechanical properties of the piezoelectric composite. The ten connectivity patterns are (0-0), (0-1), (0-2), (0-3), (1-1), (1-2), (2-2), (1-3), (2-3), and (3-3), where the first digit within the parenthesis refers to the number of dimensions of connectivity for the piezoelectric active phase and the second digit is used for the other phase. This convention can be extended to include a third phase by adding a third number within the parenthesis.

For this work, the first and third phases are piezoelectric and conductive materials that are distributed within the host matrix, while the second phase is matrix material that is self-connected in three dimensions. Analytical expressions for the effective dielectric constant of a 0-3 composite have been developed by many researchers [20–24]. Among these, three popular models are those developed by Jayasundere and Smith [24], Bruggeman [21], and Poon and Shin [23]. The model developed by Jayasundere and Smith requires the dielectric constant of the piezoelectric inclusion be greater than that of the host matrix. Thus, this formula is not valid when the dielectric constant of the inclusion is less than that of the host matrix. On the other hand, Bruggeman's model is valid for inclusions having any dielectric constant but is limited due to its nonlinear and implicit nature. Poon and Shin [23] developed a simple explicit formula for the estimation the effective dielectric constant of a 0-3 composite, wherein the inclusions must be uniformly distributed and separated from each other. In this model, it was assumed the electric displacement of a single particle was due to the effect of both the matrix and the polarization of the inclusions distributed uniformly inside the matrix.

Here, we derive an analytical expression for the prediction of the effective dielectric constant of a three phase 0-3-0 ferroelectric composite, which has not to our knowledge been done before. In our model, we assume the first and third phase inclusions are

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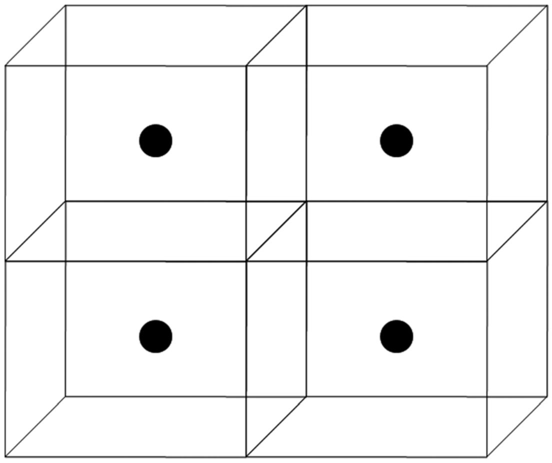

Fig. 1 Representation of uniformly distributed and separated spherical inclusions inside the matrix

uniformly distributed and separated from each other. The results for the analytical model are then compared with the experimental results from Nan et al. [5]. The shape of a dispersed particle plays a very important role in the effective dielectric constant of a conductor-dielectric composite [25,26]; and the deviation of the conductive particle from the spherical form results in higher dielectric constants of the composite [25–27]. Thus, we extend our analytical model to include the shape of the third phase inclusion to examine the influence of the shape (of the inclusion) on the effective dielectric constant of the composite. These results are then compared with the analytical results for spherical particles.

2 Theory

Let us consider a single spherical inclusion with dielectric constant $\in_i$ inside an infinite matrix of dielectric constant $\in_m$, as depicted in Fig. 1. In a two phase 0-3 composite, the inclusions are considered to be uniformly distributed and dispersed within the matrix, which is considered to be a continuum medium. This 0-3 composite can be considered as an isotropic material [28]. The 0-3-0 material we investigate here is shown in Fig. 2, wherein the third phase of 0-3-0 composite is assumed to be spherical conductive inclusions uniformly distributed and separated in the continuum of the isotropic 0-3 composite matrix.

We first consider a 0-3 composite material when an external field is applied across the z-axis. Here, the electric field inside the matrix and that inside the inclusion are assumed to be uniform and parallel to each other. The displacement field experienced by a single particle is considered as a sum of two parts; the first part due to the infinite matrix and the other due to the polarization of all the inclusions embedded inside the infinite matrix. The effective dielectric constant, $\in_e$ of a 0-3 composite can be expressed as Ref. [23]

$$\in_e = \in_m + \phi(\in_i - \in_m)\frac{1}{\phi + \frac{1}{3}(1-\phi)\left[\frac{\in_i}{\in_m}(1-\phi)+\phi+2\right]} \tag{1}$$

where ϕ is the volume fraction of the inclusions of the first phase and $\in_m$ and $\in_i$ are the dielectric constants of the matrix and the inclusion, respectively.

We can extend the expression provided in Eq. (1) for a 0-3 composite, to include a third phase, and thus define the effective dielectric constant $\in$ of the 0-3-0 composite as

$$\in = \in_m + \phi(\in_i - \in_m)\frac{1}{\phi + \frac{1}{3}(1-\phi)\left[\frac{\in_i}{\in_m}(1-\phi)+\phi+2\right]} + \phi_1\left[\left(\in_1 - \in_m + \phi(\in_i - \in_m)\frac{1}{\phi + \frac{1}{3}(1-\phi)\left[\frac{\in_i}{\in_m}(1-\phi)+\phi+2\right]}\right) \times \frac{1}{\phi_1 + \frac{1}{3}(1-\phi_1)\left[\frac{\in_1}{\in_e}(1-\phi_1)+\phi_1+2\right]}\right] \tag{2}$$

where $\in_1$ and ϕ_1 are the dielectric constant and the volume fraction of the third phase. If the third phase of the composite is a conductive material, its dielectric constant, $\in_1$ is infinite [27]. Hence, Eq. (2) reduces to

$$\in = \in_m + \phi(\in_i - \in_m)\frac{1}{\phi + \frac{1}{3}(1-\phi)\left[\frac{\in_i}{\in_m}(1-\phi)+\phi+2\right]} + \phi_1\left[\frac{3\in_m + \phi(\in_i - \in_m)\frac{1}{\phi + \frac{1}{3}(1-\phi)\left[\frac{\in_i}{\in_m}(1-\phi)+\phi+2\right]}}{(1-\phi_1)^2}\right] \tag{3}$$

Since the shape of the conductive filler particle influences the effective dielectric constant of the 0-3-0 composite [5], we include a shape factor to take into consideration the shape and the aspect

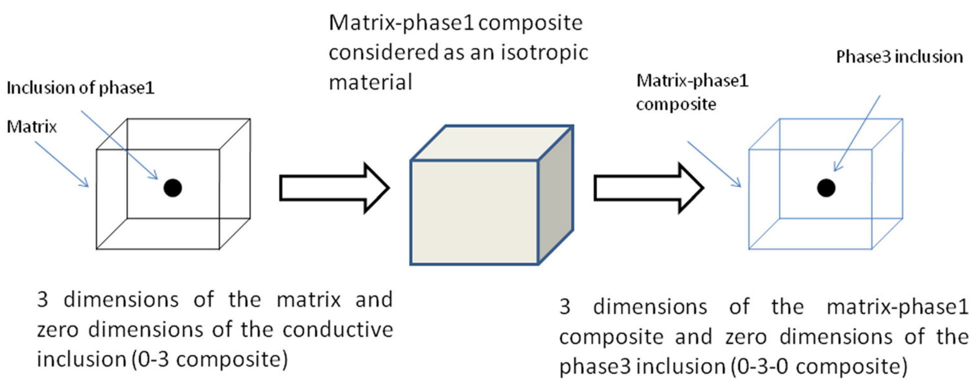

Fig. 2 Representation of a 0-3-0 composite by assuming that the 0-3 composite is an isotropic material

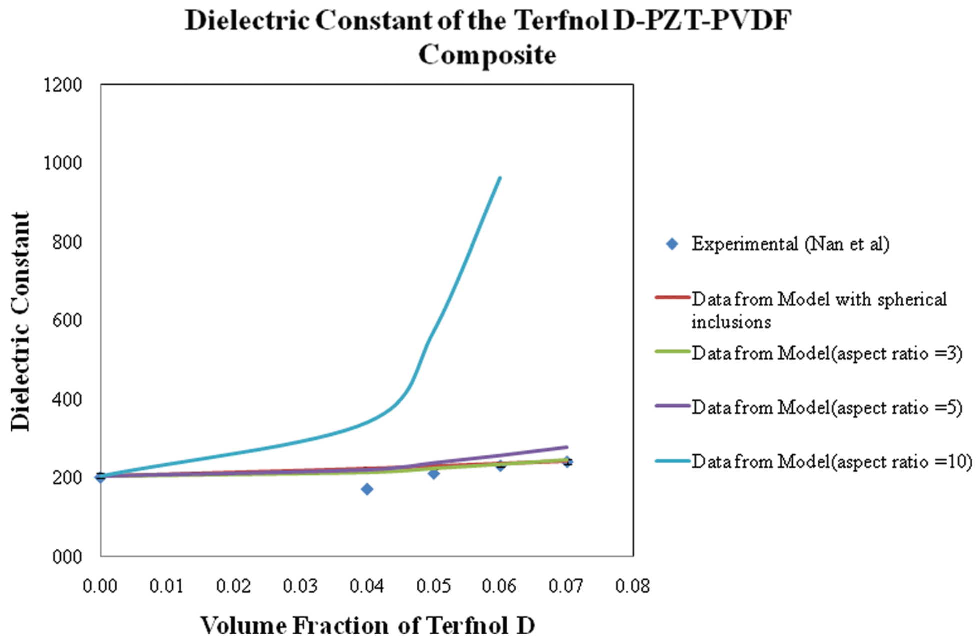

Fig. 3 Comparison of analytical model results with experimental data from Nan et al. [1]

ratio of the inclusions. If we consider the case where the first, second, and third phases in the composite are spherical for ferroelectric inclusion and matrix; and nonspherical for the conductive inclusion; the effective dielectric constant of the composite can be expressed as Ref. [27]

$$\epsilon = \left[\epsilon_m + \phi(\epsilon_i - \epsilon_m)\frac{1}{\phi + \frac{1}{3}(1-\phi)\left[\frac{\epsilon_i}{\epsilon_m}(1-\phi) + \phi + 2\right]}\right] \times [1-\phi_1]^{-B} \tag{4}$$

where B is the shape factor of the conductive particle, and defined as Refs. [27] and [29]

$$B = \frac{1}{3}\sum_{i=1,2,3} A_i^{-1} \tag{5}$$

In Eq. (5), A is the depolarization factor, which is defined according to the dimensions a, b, c of the conducting particle

$$A_j = \frac{abc}{2}\int_0^{\infty}\frac{dt}{(t+j^2)[(t+a^2)(t+b^2)(t+c^2)]^{\frac{1}{2}}} \tag{6}$$

where $j = a, b, c$.

For spheroid particles, the shape factor B, reduces to Ref. [27]

$$B = \frac{2-3A}{3A(1-2A)} \tag{7}$$

Here, for the spheroid particles $A_a = A_b = A$, $A_c = 1 - 2A$.

For an increase in aspect ratio for the spheroidal inclusion the dielectric properties of the 0-3-0 composite is enhanced [27,29]. Therefore, a deviation of the conductive inclusion size from spherical particles with aspect ratio 1 to higher aspect ratios increases the dielectric constant for the same volume fraction of the inclusion.

3 Results and Discussion

The analytical expression for the effective dielectric constant was determined using Eqs. (3) and (4) and compared with experimental data from Nan et al. [5] in Fig. 3. Here, the three phase 0-3-0 composite under consideration is PZT - PVDF - (Terfenol-D) where Terfenol-D is the conducting phase and thus, the third phase for our model. Both the PZT and Terfenol-D inclusions are of micron size.

The effective dielectric constant calculated from Eq. (3), the experimental data and the data from the linear best fit to the experimental data are presented in Fig. 3. The predicted values for effective dielectric constant compare well with the experimental data up to a volume fraction of 0.7 of the conducting phase of Terfenol-D, where the composite is in the percolation transition region. When the composite is in the percolation transition region and volume fraction of the conductive inclusion goes above the percolation limit; the composite ceases to be a 0-3-0 composite due to the formation of several percolation paths. Our model does not take the percolation transition into consideration. Thus, this model is valid until the volume fraction of the conductive inclusion reaches the percolation transition.

In order to examine the influence of conductive inclusion shape on the effective dielectric constant of the composite, we have used our model Eq. (4) to predict these values for the PZT- PVDF- conductive inclusion composite with aspect ratios of 1, 3, 5, and 10 for the conducting phase inclusions. Comparison of these results with those for spherical conductive inclusions, are depicted in Fig. 3, and indicate an increase in aspect ratio enhances the dielectric properties of the 0-3-0 composites significantly. For example, for a conductive inclusion volume fraction of 0.06, the dielectric constant increases from 242 (spherical inclusion) to 266, 317, and 604 for aspect ratios equal to 3, 5, and 10, respectively. The dielectric properties of the composite increase significantly with the increase in the aspect ratio of the conducting inclusion from 5 to 10. This supports the conclusions drawn in previous experimental studies [5]. This analytical study does not, however, consider the effect of shape/aspect ratio on the percolation of the 0-3-0 composite.

A comparison of the three phase model with the values of the dielectric constant of the three phase $BaTiO_3$-PVDF-MWNT (multiwalled carbon nanotube) is shown in Fig. 4. Here, the

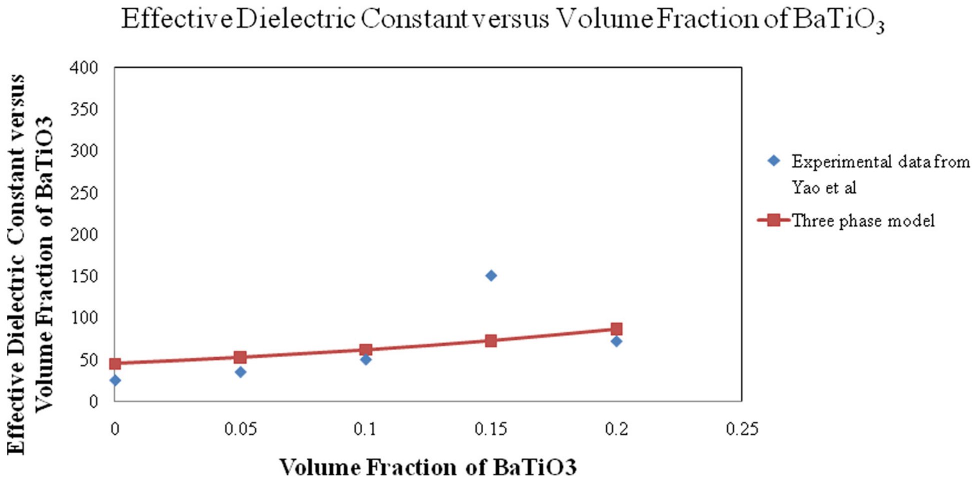

Fig. 4 A comparison of the three phase model with the values of the dielectric constant of the three phase $BaTiO_3$-PVDF-MWNT

spheroidal conductive inclusions are MWNTs. The predicted values from the three phase model compare well with the experimental data except for $BaTiO_3$ volume fraction = 0.15 where the variation can be attributed to MWNT polarization, which the model does not take into account [11].

4 Conclusion

Analytical expressions for the estimation of the effective dielectric constant of a 0-3-0 composite have been derived for both spherical and spheroidal conductive inclusions. Here, we consider the 0-3 composite as an isotropic material and then evaluate the effective dielectric constant of the 0-3-0 composite by assuming spherical/spheroidal inclusions of the third phase in the 0-3 composite matrix. The derived expression for the spherical conductive inclusion is validated favorably with experimental values from Nan et al. [5]. The analytical model is compared to experimental results where the conductive filler material is comprised of micron sized particles. However, the influence of conductive material particle size on the effective dielectric constant is yet to be determined.

The derived expression for the spheroidal conductive inclusions is used for an analytical study on the effect of inclusion shape of the conducting phase reveals the importance of shape/aspect ratio of the inclusions on the effective dielectric constant of the composite. A comparison of the analytical predictions with the experimental values from Yao et al. [14], validates the three phase analytical model for 0-3-0 composites with spheroidal conductive inclusions. The investigated aspect ratios are in keeping with commercially available nanofibers and nanowhiskers, which can range in aspect ratio from 20 to 600. Future work will include the extension of the above analytical model to estimate the piezoelectric strain coefficient.

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