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New explicit formulas for the effective piezoelectric coefficients of binary 0-3 composites

C. H. Ho · Y. M. Poon · F. G. Shin

Abstract The explicit formula for the effective dielectric constant of binary 0-3 composites (Poon and Shin, J. Mat. Sc. **39** (2004) 1277–1281) is extended into two explicit formulas for the prediction of the elastic properties of macroscopically isotropic 0-3 composites. By combining them with the explicit effective dielectric formula into a calculation scheme (Wong et al., J. Appl. Phys. **90** (2001) 4690), we obtained two new explicit formulas for the prediction of the d_{31} and d_{33} values for binary 0-3 piezoelectric composites. These two explicit formulas are applicable even when the inclusion volume fraction is high. Comparing with existing experimental data, they are found to fit more favorably than those predicted by Wong et al. and others. Also, being explicit makes these formulas much easier to be embedded into other effective property calculations for binary 0-3 composite materials.

Keywords Explicit formula · Effective piezoelectric coefficients · 0-3 composites

Introduction

Theoretical and empirical models for the prediction of the effective piezoelectric coefficients of 0-3 composites have been developed by many researchers [e.g. 1–4]. The models of Furukawa [1–3], Jayasundere [4] and Wong et al. [5] are three typical approaches. In Furukawa's model, both the inclusion and the matrix are assumed to be incompressible. When compared with experimental results of d_{31} of PZT/PVDF composites [3], Furukawa's model shows good agreement with experimental values only for dilute suspension of the inclusions (volume fraction ϕ less than about 0.3). The model developed by Jayasundere does not fit with the d_{33} experimental data of $PbTiO_3$/P(VDF/TeFE) composites [6]. In addition, Jayasundere model does not give correct limits when the volume fraction of the inclusions, ϕ, tends to zero or tends to one. For higher inclusion volume fractions, explicit expressions are derived by Wong et al. [5]. Their derivation starts from a single spherical inclusion problem, for which the associated elastic problem has already been solved by Goodier [7]. The solution is adopted for the dilute suspension case, assuming that the interactions between the inclusions can be neglected. Explicit formulas of the effective piezoelectric coefficients (d_{31} and d_{33}) are then derived in terms of the dielectric, elastic and piezoelectric properties of the inclusion and the matrix material. The expressions obtained are then extended for non-dilute suspension of inclusions by using formulas for the effective dielectric constant, effective bulk modulus and shear modulus that are known to be applicable for non-dilute cases. When compared with experimental data, their formulas give reasonably good fitting for higher volume fractions.

As in practical applications of the piezoelectric 0-3 composites, usually high volume fractions of the inclusions are employed. Therefore it is the aim of this article to derive explicit formulas for d_{31} and d_{33} effective piezoelectric coefficients of the composites that give reasonable predicted values even at high volume fractions of the inclusions.

The following is the structure of this article. In Section 2, the idea employed earlier (Poon and Shin [8]) for finding an explicit formula for the effective dielectric constant of

C. H. Ho · Y. M. Poon (✉)
Department of Applied Physics and Materials Research Centre,
The Hong Kong Polytechnic University, Hong Kong
e-mail: apaympoo@inet.polyu.edu.hk

F. G. Shin
Centre for Smart Materials, The Hong Kong Polytechnic University, Hong Kong

binary 0-3 composites is applied for treating elastic problems. This results in two explicit formulas for the effective elastic coefficients. By incorporating them into the explicit effective dielectric formula given in [8], and plugging all into the scheme of Wong et al. [5], two explicit formulas for the prediction of the effective piezoelectric d_{31} and d_{33} coefficients for binary 0-3 piezoelectric composites are obtained. In Section 3, these two new formulas, when compared with experimental data, are shown to fit more favorably than those predicted by Wong et al. [5] and others, especially in the high volume fraction region. The last section is the discussion and conclusions section.

Theory

Effective dielectric constant

Poon and Shin [8] considered the single inclusion electrical problem of a single dielectric spherical inclusion with dielectric constant ε_i embedded in an infinite matrix with dielectric constant ε_m . When an external electric field is applied along the z-axis, and suppose E_m is the electric field in the matrix region far away from the inclusion, then the electric field E_i inside the inclusion, is uniform and is parallel to E_m [5]. The relationship between the electric fields E_i and E_m, and the corresponding electric displacements D_i and D_m is given by [5]

$$D_i - D_m = -2\varepsilon_m(E_i - E_m) \tag{1}$$

Defining δD as $D_i - D_m$ and δE as $E_i - E_m$, it can be written in the form:

$$\delta D = -2\varepsilon_m \delta E \tag{2}$$

Poon and Shin [8] have shown that, one way to take into account the interaction between the inclusions is to add an extra term:

$$\Delta D = -2\varepsilon_m \Delta E + \phi(\varepsilon_i - \varepsilon_m)\langle E_i\rangle \tag{3}$$

where $\Delta D \equiv \langle D_i\rangle - \langle D_m\rangle$, $\Delta E \equiv \langle E_i\rangle - \langle E_m\rangle$
After some manipulation, the effective dielectric constant ε of the composite is found:

$$\varepsilon = \varepsilon_m + \phi(\varepsilon_i - \varepsilon_m)\frac{1}{\phi + (1-\phi)\frac{\varepsilon_i + 2\varepsilon_m - \phi(\varepsilon_i - \varepsilon_m)}{3\varepsilon_m}} \tag{4}$$

where ϕ is the volume fraction of the inclusions.

Effective elastic coefficients

For elastic properties, we can, by analogy, replace the electric displacement D by the stress σ and the electric field E by the strain e. For the single inclusion elasticity problem of a single spherical inclusion having bulk modulus k_i and shear modulus μ_i in an infinite matrix having bulk modulus k_m and shear modulus μ_m , subjected to a uniform external stress along the z-axis, Goodier [7] has worked out the analytical solutions for the displacements and the stresses inside the inclusion and in the matrix, in spherical coordinates. By transforming Goodier's solution to Cartesian coordinates, it can be shown that

$$\begin{aligned} \delta\sigma_1 &= A\delta e_1 + B\delta e_2 + B\delta e_3 \\ \delta\sigma_2 &= B\delta e_1 + A\delta e_2 + B\delta e_3 \\ \delta\sigma_3 &= B\delta e_1 + B\delta e_2 + A\delta e_3 \end{aligned} \tag{8}$$

where

$$\delta\sigma_j \equiv \sigma_{ij} - \sigma_{mj}, \quad \delta e_j \equiv e_{ij} - e_{mj} \quad (j = 1, 2 \text{ or } 3) \tag{9}$$

Here the first subscripts i and m refer to the inclusion and the matrix respectively, and the second subscripts 1, 2 and 3 refer to the x-axis, y-axis and z-axis directions, respectively.

$$\begin{aligned} A &= \frac{10}{9}\mu_m\left(-3 + \frac{2\mu_m}{k_m + 2\mu_m}\right), \\ B &= \frac{1}{9}\mu_m\left(-3 - \frac{10\mu_m}{k_m + 2\mu_m}\right) \end{aligned} \tag{10}$$

Similar to the electrical case, when there are several inclusions inside the matrix, one way to take into account the interaction between them is adding additional terms.

$$\begin{pmatrix} \Delta\sigma_1 \\ \Delta\sigma_2 \\ \Delta\sigma_3 \end{pmatrix} = \begin{pmatrix} A & B & B \\ B & A & B \\ B & B & A \end{pmatrix}\begin{pmatrix} \Delta e_1 \\ \Delta e_2 \\ \Delta e_3 \end{pmatrix} + \phi\begin{pmatrix} C & D & D \\ D & C & D \\ D & D & C \end{pmatrix}\begin{pmatrix} \langle e_{i1}\rangle \\ \langle e_{i2}\rangle \\ \langle e_{i3}\rangle \end{pmatrix} \tag{11}$$

where $\Delta\sigma_j \equiv \langle\sigma_{ij}\rangle - \langle\sigma_{mj}\rangle$, $\Delta e_j \equiv \langle e_{ij}\rangle - \langle e_{mj}\rangle$ (j = 1, 2 or 3)
$\langle x\rangle$ denotes the volumetric average of the physical quantity x over the respective material and

$$\begin{aligned} C &\equiv (k_i - k_m) + \frac{4}{3}(\mu_i - \mu_m), \\ D &\equiv (k_i - k_m) - \frac{2}{3}(\mu_i - \mu_m) \end{aligned} \tag{12}$$

Since the 0-3 composite, as a whole, is an isotropic material, its elastic behavior can be described by just two coefficients, for example, the effective bulk modulus k and the effective shear modulus μ. They are defined by the stress-strain relationship

$$\begin{pmatrix} \langle\sigma_1\rangle \\ \langle\sigma_2\rangle \\ \langle\sigma_3\rangle \end{pmatrix} = \begin{pmatrix} E & F & F \\ F & E & F \\ F & F & E \end{pmatrix} \begin{pmatrix} \langle e_1\rangle \\ \langle e_2\rangle \\ \langle e_3\rangle \end{pmatrix} \tag{13}$$

where

$$E \equiv k + \frac{4}{3}\mu, \quad F \equiv k - \frac{2}{3}\mu \tag{14}$$

Using Eqs. (8) to (14), and the following relationships,

$$\langle\sigma_j\rangle = \phi\langle\sigma_{ij}\rangle + (1-\phi)\langle\sigma_{mj}\rangle \quad j = 1, 2, 3 \tag{15}$$

$$\langle e_j\rangle = \phi\langle e_{ij}\rangle + (1-\phi)\langle e_{mj}\rangle \quad j = 1, 2, 3 \tag{16}$$

the effective bulk modulus k and the effective shear modulus μ of the composite can be found:

$$k = k_m + \frac{\phi(k_i - k_m)(k_m + \frac{4}{3}\mu_m)}{(1-\phi)\left[k_m + \frac{4}{3}\mu_m + (1-\phi)(k_i - k_m)\right] + \phi\left(k_m + \frac{4}{3}\mu_m\right)} \tag{17}$$

$$\mu = \mu_m + \frac{\phi(\mu_i - \mu_m)\frac{5\mu_m(3k_m+4\mu_m)}{6(k_m+2\mu_m)}}{(1-\phi)\left[\frac{5\mu_m(3k_m+4\mu_m)}{6(k_m+2\mu_m)} + (1-\phi)(\mu_i - \mu_m)\right] + \phi\frac{5\mu_m(3k_m+4\mu_m)}{6(k_m+2\mu_m)}} \tag{18}$$

Effective piezoelectric coefficients

Wong et al. [5, 11] have given explicit formulas for the effective piezoelectric d_{31} and d_{33} coefficients of 0-3 composites:

$$d_{31} = \phi F_E[(F_T^{\perp} + F_T^{||})d_{31i} + F_T^{\perp} d_{33i}] + (1-\phi)\overline{F}_E[(\overline{F}_T^{\perp} + \overline{F}_T^{//})d_{31m} + \overline{F}_T^{\perp} d_{33m}] \tag{19}$$

$$d_{33} = \phi F_E[2F_T^{\perp} d_{31i} + F_T^{//} d_{33i}] + (1-\phi)\overline{F}_E[2\overline{F}_T^{\perp} d_{31m} + \overline{F}_T^{//} d_{33m}] \tag{20}$$

where the "electric field factors" are

$$F_E \equiv \frac{1}{\phi}\frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \tag{21}$$

$$\overline{F}_E \equiv \frac{1}{1-\phi}\frac{\varepsilon_i - \varepsilon}{\varepsilon_i - \varepsilon_m} \tag{22}$$

and the "stress field factors" are defined to be

$$F_T^{\perp} \equiv \frac{1}{\phi}\left(\frac{1}{3}\frac{\frac{1}{k} - \frac{1}{k_m}}{\frac{1}{k_i} - \frac{1}{k_m}} - \frac{1}{3}\frac{\frac{1}{\mu} - \frac{1}{\mu_m}}{\frac{1}{\mu_i} - \frac{1}{\mu_m}}\right) \tag{23}$$

$$F_T^{//} \equiv \frac{1}{\phi}\left(\frac{1}{3}\frac{\frac{1}{k} - \frac{1}{k_m}}{\frac{1}{k_i} - \frac{1}{k_m}} + \frac{2}{3}\frac{\frac{1}{\mu} - \frac{1}{\mu_m}}{\frac{1}{\mu_i} - \frac{1}{\mu_m}}\right) \tag{24}$$

$$\overline{F}_T^{\perp} \equiv \frac{1}{1-\phi}\left(\frac{1}{3}\frac{\frac{1}{k_i} - \frac{1}{k}}{\frac{1}{k_i} - \frac{1}{k_m}} - \frac{1}{3}\frac{\frac{1}{\mu_i} - \frac{1}{\mu}}{\frac{1}{\mu_i} - \frac{1}{\mu_m}}\right) \tag{25}$$

$$\overline{F}_T^{//} \equiv \frac{1}{1-\phi}\left(\frac{1}{3}\frac{\frac{1}{k_i} - \frac{1}{k}}{\frac{1}{k_i} - \frac{1}{k_m}} + \frac{2}{3}\frac{\frac{1}{\mu_i} - \frac{1}{\mu}}{\frac{1}{\mu_i} - \frac{1}{\mu_m}}\right) \tag{26}$$

They have taken the dielectric constant ε in the electric field factors as given by the Bruggeman formula [12]

$$\frac{\varepsilon_i - \varepsilon}{\varepsilon^{\frac{1}{3}}} = (1-\phi)\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_m^{\frac{1}{3}}} \tag{27}$$

and the bulk k and shear μ modulus in the stress field factors by the Hashin model [10].

Using the same scheme, but employing the new formula (Eq. (4)) for the effective dielectric constant and the new formulas (Eqs. (17) and (18)) for the effective elastic coefficients, we obtained therefore two new explicit equations for the two effective piezoelectric coefficients d_{31} and d_{33}.

Comparison with experimental data

Effective elastic coefficients

Predictions of the effective bulk modulus and the effective shear modulus using the two explicit formulas (17) and (18) are compared with the experimental data given by Smith [9]. The composite considered is a matrix of epoxy embedded with glass spheres. The Poisson's ratios of the glass (ν_i) and the epoxy (ν_m) are 0.23 and 0.394 respectively and the Young's moduli of the glass (Y_i) and the epoxy (Y_m) are 76.0 GPa and 3.01 GPa respectively. Figure 1 shows the comparison for the bulk modulus, in which we have plotted predictions based on our model and the Hashin model [10]. The bulk modulus of Hashin's model is given by

$$k = k_m + \frac{\phi(k_i - k_m)}{1 + (1-\phi)\frac{k_i - k_m}{k_m + \frac{4}{3}\mu_m}} \tag{28}$$

At low volume fractions of the glass spheres, both Hashin's model and our model give good agreement with

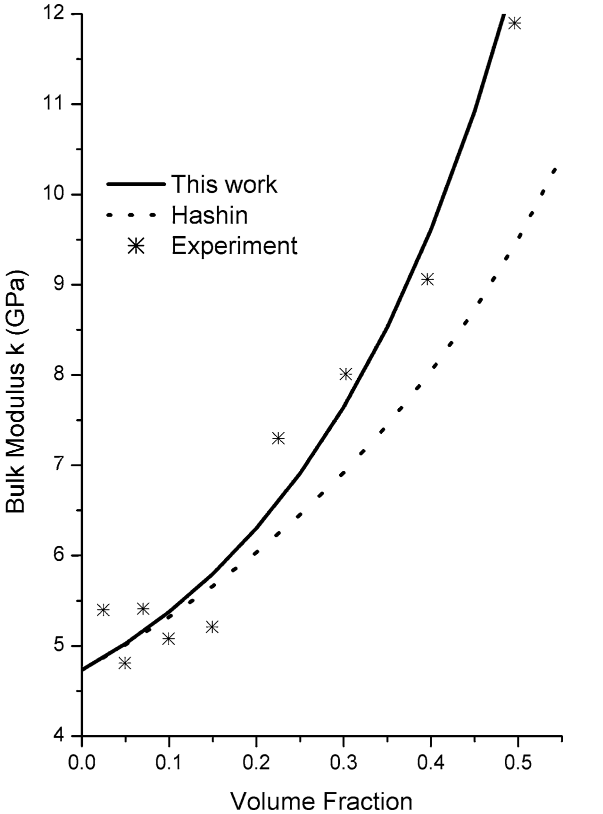

Fig. 1 Comparison of the effective bulk modulus predicted by this work (Eq. (17)) and Hashin's model (Eq. (28)) with experimental data of Smith [9]

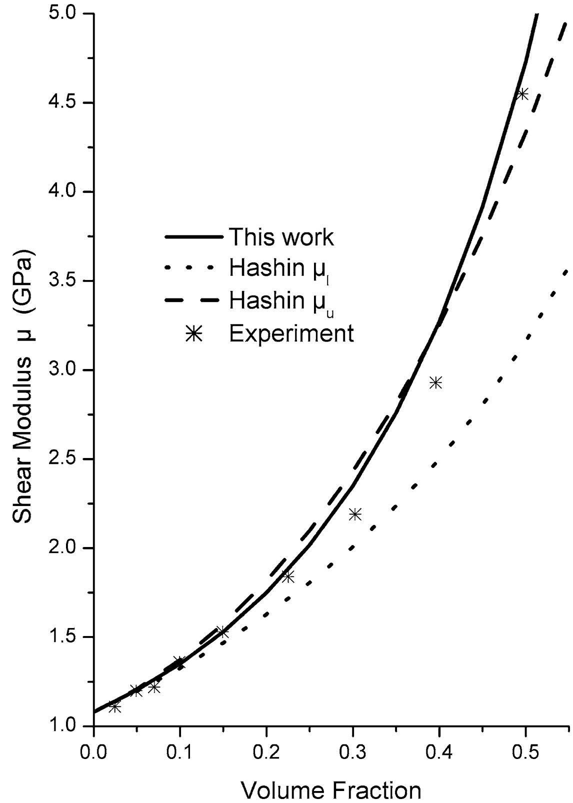

Fig. 2 Comparison of the effective shear modulus predicted by this work (Eq. (18)), lower bound of shear modulus of Hashin model, μ_l (Eq. (29)) and upper bound of shear modulus of Hashin model, μ_u (Eq. (30)) with experimental data of Smith [9]

the experimental data. However, at higher volume fractions, the Hashin model underestimates the effective bulk modulus while our model still fits relatively well to the experimental data.

Figure 2 shows the comparison for the shear modulus. Hashin's model gives lower bound μ_l and upper bound μ_u as follows:

$$\mu_l = \mu_m \left(1 + \frac{15(1-\nu_m)\left(\frac{\mu_i}{\mu_m}-1\right)\phi}{7-5\nu_m+2(4-5\nu_m)\left(\frac{\mu_i}{\mu_m}-\left(\frac{\mu_i}{\mu_m}-1\right)\phi\right)}\right) \quad (29)$$

$$\mu_u = \mu_m\left[1+\left(\frac{\mu_i}{\mu_m}-1\right)\frac{B_1}{A_1+B_1C_1}\phi\right] \quad (30)$$

where

$A_1 \equiv \frac{42}{5\mu_m}\frac{\mu_m-\mu_i}{1-\nu_m}\phi(\phi^{\frac{2}{3}}-1)^2\vartheta$, $B_1 \equiv [(7-10\nu_i) \; -(7-10\nu_m)\vartheta]4\phi^{\frac{7}{3}} + (7-10\nu_m)\vartheta$

$$C_1 \equiv \frac{\mu_i}{\mu_m} + \frac{7-5\nu_m}{15(1-\nu_m)}\left(1-\frac{\mu_i}{\mu_m}\right) + \frac{2(4-5\nu_m)}{15(1-\nu_m)}\left(1-\frac{\mu_i}{\mu_m}\right)\phi$$

and

$$\vartheta \equiv \frac{(7+5\nu_i)\mu_i + 4(7-10\nu_i)\mu_m}{35(1-\nu_m)\mu_m} \quad (31)$$

At low volume fractions, both bounds of Hashin's model and our model give reasonable predicted values when compared with the experimental data. However, when the volume fraction of the inclusions is higher, the lower bound of Hashin's model fails to give reasonable predictions, while its upper bound and our model still show good agreement with the experimental data.

Effective piezoelectric coefficients

Equations (19) and (20) calculated using our scheme, the scheme adopted by Wong et al.'s paper [5] and other models are compared with experimental data given by Furukawa [3] and Zou et al. [6] (Figs. 3 and 4).

Figure 3 shows the d_{31} comparison for PZT/PVDF system [3]. The Poisson's ratios of the PZT inclusion and the matrix are 0.3 and 0.4 respectively and the Young's moduli of the inclusion and the matrix are 58.7 GPa and

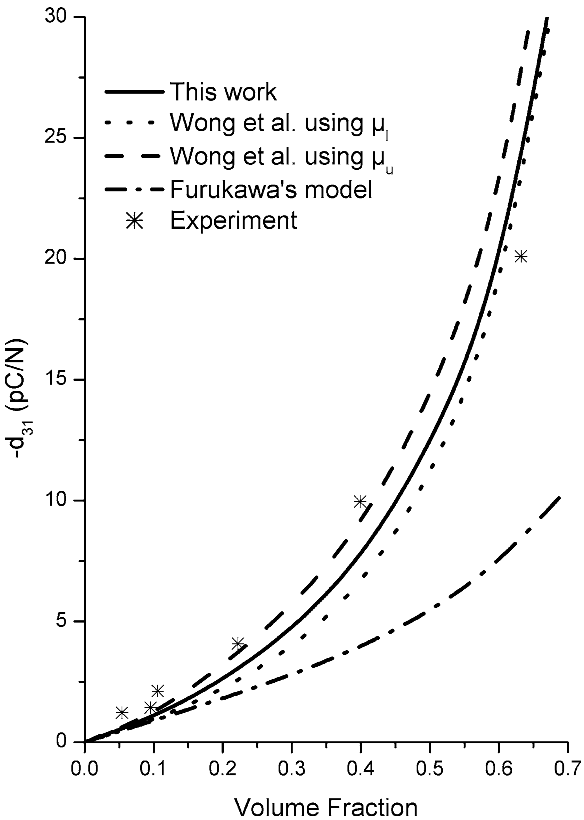

Fig. 3 Predictions of the effective piezoelectric coefficient d_{31} by this work (Eq. (19)), Wong et al.'s model [5] using lower and upper bounds of shear modulus of Hashin [10] and Furukawa's model [1]. Experimental data are taken from [3] of Furukawa

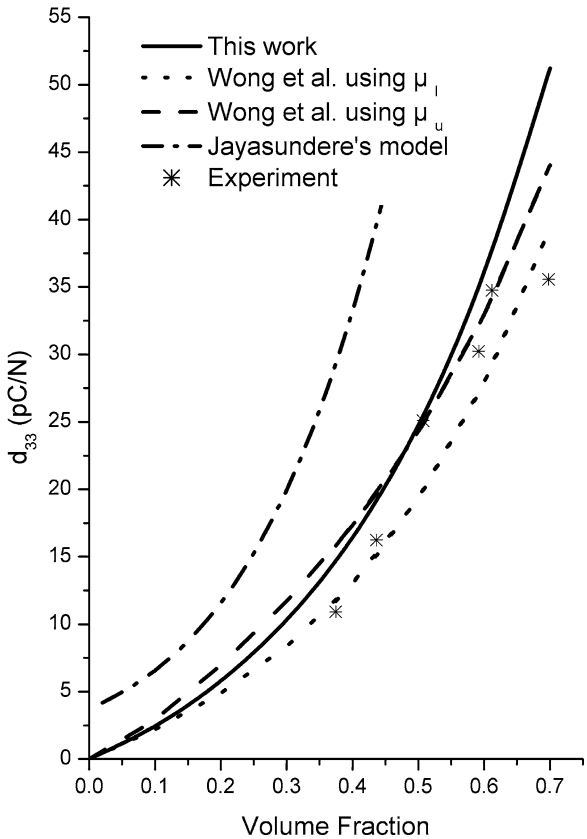

Fig. 4 Predictions of the effective piezoelectric coefficient d_{31} by this work (Eq. (19)), Wong et al.'s model [5] using lower and upper bounds of shear modulus of Hashin [10] and Jayasundere's model [4]. Experimental data are taken from [6] of Zou et al.

2.52 GPa respectively. The dielectric constants are 1900 for the inclusion and 14 for the matrix. The d_{31} and d_{33} values for the inclusion are -180 pC/N and 450 pC/N respectively. For dilute suspension cases, our scheme and the scheme of Wong et al. using μ_u show similar performance, while the Furukawa model underestimates the piezoelectric coefficient. At higher volume fractions, the Furukawa model fails obviously, while the other schemes show similar performance.

Figure 4 shows d_{33} comparisons of different models with the experimental values for $PbTiO_3$/P(VDF/TeFE) system [6], in which experimental data are available only at high volume fractions. The Poisson's ratios of the inclusion and the matrix are 0.22 and 0.4 respectively and the Young's moduli of the inclusion and the matrix are 126.7 GPa and 2.81 GPa respectively. The d_{31} and d_{33} values for the inclusion are -9.5 pC/N and 94 pC/N respectively. The dielectric constants are 150 for the inclusion and 6 for the matrix. In this case, almost all experimental data fall within the bounds of Wong et al. [5] and our scheme fits reasonably good to the data. On the other hand, the Jayasundere model [4] obviously overestimates the coefficient.

We would like to emphasis here that the Wong et al. [5] scheme using μ_l and μ_u provide the lower and upper bounds for the prediction of the effective piezoelectric coefficients of the composite. As shown in these comparisons, we do not know beforehand which bound gives better predicted values. In this sense, our model has the merit that it always gives reasonable predictions, no matter the volume fraction is low or high.

Discussion and conclusions

By using the new dielectric constant formula given by Poon and Shin [8] and the new bulk and shear modulus formulas derived in this work, we obtained two new explicit formulas for the effective piezoelectric coefficients, d_{31} and d_{33}. For the dilute suspension cases, they give values similar with other theoretical models. However, at higher volume fractions, they give better predictions when compared with typical experimental data available in the literature.

In this article, we have derived two explicit formulas for the effective bulk modulus and the effective shear modulus of 0-3 composites, based on Goodier's solution [7] and the approach used in the article of Poon and Shin [8]. The same idea will next be applied to find explicit formulas for the effective elastic coefficients of 1-3 composite materials.

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References

1. T. Furukawa, K. Fujino, and E. Fukada, *Jpn. J. Appl. Phys.*, **15**, 2119 (1976).
2. T. Furukawa, K. Fujino, and E. Fukada, *J. Appl. Phys.*, **50**, 4904 (1979).
3. T. Furukawa, *IEEE Trans. Electr. Insul.*, **24**, 375 (1989).
4. N. Jayasundere, B.V. Smith, and J.R. Dunn, *J. Appl. Phys.*, **76**(5) (1994).
5. C.K. Wong, Y.M. Poon, and F.G. Shin, *J. Appl. Phys.*, **90**, 4690 (2001).
6. X. Zou, L. Zhang, X. Yao, L. Wang, and F. Zhang, in *Proceedings of the Tenth IEEE International Symposium on Applications of Ferroelectrics 1996*, (1996) vol. 2, p. 1023
7. J.N. Goodier, *Trans. ASME,* **55**, 39 (1933).
8. Y.M. Poon, and F.G. Shin, *J. Materials Sci.*, **39**, 1277 (2004).
9. J.C. Smith, *J. Research of the National Bureau of Standards*, **80A**(1) 45 (1976).
10. Z. Hashin, *J. Appl. Mech.*, **29**, 143 (1962).
11. C.K. Wong, *Effective Piezoelectric Properties of Ferroelectric 0-3 composites* (MPhil. Thesis, The Hong Kong Polytechnic University, 2002) p. 31.
12. D.A.G. Bruggeman, *Ann. Phys. Lpz.*, **24**, 635 (1935).