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A simple explicit formula for the effective dielectric constant of binary 0-3 composites

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We have derived a simple, analytic formula for the prediction of the effective dielectric constant of binary 0-3 composite materials. In comparison with a popular formula in the field (Jayasundere and Smith [1]), it gives the expected asymptotic value for the internal electric field of the inclusions when their total volume fraction tends to one. It is also applicable to the whole range of the volume fraction of the inclusions and is reasonably good for all values of the dielectric constants of the constituents. For non-conductive constituents, it gives effective complex permittivity prediction that fits well to experimental data, out-performs the Jayasundere-Smith formula and a linearized version [2, 3] of the well-known Bruggeman formula. © *2004 Kluwer Academic Publishers*

1. Introduction

In a two-phase composite (i.e., a binary composite), each phase may be spatially self-connected in zero, one, two, or three dimensions, thus giving many different combinations of phase connectivity, which are usually indicated by two numbers denoting the connectivity of the filler and that of the host matrix, respectively. For example, a particulate-filled composite can be denoted as a 0-3 composite.

The effective dielectric constant of a 0-3 composite has been studied by many researchers [4–6]. Among those, Jayasundere and Smith formula [1] is a popular one [7–9]. It is an analytic formula for the effective dielectric constant ε of a binary 0-3 composite, derived by modifying the well-known Kerner expression [4] to include interactions. The developed expression, which is valid when $\varepsilon_i \gg \varepsilon_m$, where ε_i and ε_m is the dielectric constant of the inclusion and the matrix respectively, is a function of the volume fraction ϕ of the inclusions:

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

The predictions given by this formula compare favorably with experimental data for piezoelectric ceramic inclusions in a dielectric continuum having differing dielectric constants [7–9].

However, we find that as an intermediate step in their derivation, they have expressed the total electric field $\vec{E}_i$ inside a spherical inclusion in terms of the applied field $\vec{E}_o$ by the following formula:

$$\vec{E}_i = \frac{3\varepsilon_m}{\varepsilon_i + 2\varepsilon_m}\left(1 + 3\phi\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m}\right)\vec{E}_o \tag{2}$$

We note that when ϕ tends to one, the above expression does not give $\vec{E}_i = \vec{E}_o$, the expected asymptotic value.

Also, as mentioned above, the formula is not valid when $\varepsilon_i < \varepsilon_m$.

Another formula which is widely used in the 0-3 composite field is that of Bruggeman [5]:

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

This is an implicit formula for ε. In order to find ε, one has to solve a non-linear equation. This limits its uses in situations where a simple, explicit expression is more desirable.

It is the aim of this work to develop such a formula for ε that gives reasonably good predictions for most situations.

The following is the structure of this article. In Section 2, the electric displacement in a typical inclusion is approximated to be the sum of that due to the medium and that due to other inclusions treated as a matrix of randomly distributed electric dipoles. A simple analytic formula for the prediction of the effective dielectric constant for binary 0-3 composite materials is then derived. In Section 3, we compare the predictions calculated by this formula with experimental data, the Jayasundere and Smith formula and the Bruggeman formula. For the cases that $\varepsilon_i < \varepsilon_m$, we compare, in Section 4, our predictions to simulated data obtained using numerical methods. Then in Section 5, we extend our formula for the prediction of the effective complex permittivity and compare the results to experimental data, the complex version of the Jayasundere and Smith formula, as well as to a linearized version of

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the Bruggeman formula. Some conclusions are made in the last section.

2. Theory

Consider a particulate-filled composite material composed of dielectric spheres with dielectric constant ε_i dispersed in a continuum medium with dielectric constant ε_m.

Suppose the external electric field is $\vec{E}_o$ along the z-axis, it can be shown that as long as the inclusions are uniformly distributed or are well separated from one another, the electric field $\vec{E}_i$ inside each inclusion is uniform and is parallel to $\vec{E}_o$. Also, the polarization of each inclusion, $\vec{P}_i$, is related to the internal electric field $\vec{E}_i$ by the following equation:

$$\vec{P}_i = (\varepsilon_i - \varepsilon_m)\vec{E}_i \tag{4}$$

Now we consider the electric displacement $\vec{D}'_m$ as seen by a particular single inclusion to be the sum of two parts: one due to the pure medium and the other due to the total polarization $\vec{P}$ of all other inclusions taken as "smeared out" uniformly within the medium:

$$\vec{D}'_m = \varepsilon_m \vec{E}_m + \vec{P} \tag{5}$$

We have $\vec{P} = \phi\vec{P}_i$, where ϕ is the volume fraction of the inclusions.

Therefore, by using Equations 4 and 5, we get

$$\vec{D}'_m = \varepsilon_m\vec{E}_m + \phi\vec{P}_i = \varepsilon_m\vec{E}_m + \phi(\varepsilon_i - \varepsilon_m)\vec{E}_i \tag{6}$$

For a single inclusion, as long as $\vec{P}$ is a constant, we have [10],

$$\vec{D}_i + 2\varepsilon_m(\vec{E}_i - \vec{E}_m) = \vec{D}'_m \tag{7}$$

Here $\vec{D}_i = \varepsilon_i\vec{E}_i$ is the electric displacement inside an inclusion.

From Equations 6 and 7, we get

$$[\varepsilon_i + 2\varepsilon_m - \phi(\varepsilon_i - \varepsilon_m)]\vec{E}_i = 3\varepsilon_m\vec{E}_m \tag{8}$$

Note that $\vec{E}_o = \phi\vec{E}_i + (1-\phi)\vec{E}_m$ and therefore when $\phi = 1$, Equation 8 gives $\vec{E}_i = \vec{E}_o$, the correct asymptotic value.

Consider the volumetric average of the quantity $\vec{Q} \equiv \vec{D} - \varepsilon_m\vec{E}$, where $\vec{D}$ is the displacement vector and $\vec{E}$ is the electric field:

$$\begin{aligned}\langle\vec{Q}\rangle &= \frac{1}{V}\int_V \vec{Q}\,\mathrm{d}V = \frac{1}{V}\int_V (\vec{D} - \varepsilon_m\vec{E})\,\mathrm{d}V \\ &= \langle\vec{D}\rangle - \varepsilon_m\langle\vec{E}\rangle\end{aligned} \tag{9}$$

where $\langle x\rangle$ denotes the volumetric average of the physical quantity x over the whole composite.

Since at each point in the matrix material, we have $\vec{D}_m = \varepsilon_m\vec{E}_m$ and hence $\vec{Q} = 0$ inside the matrix, and we can write

$$\begin{aligned}\langle\vec{Q}\rangle &= \frac{1}{V}\int_{V_i} (\vec{D}_i - \varepsilon_m\vec{E}_i)\,\mathrm{d}V = \frac{1}{V}\int_{V_i} (\varepsilon_i\vec{E}_i - \varepsilon_m\vec{E}_i)\,\mathrm{d}V \\ &= \phi(\varepsilon_i - \varepsilon_m)\vec{E}_i\end{aligned} \tag{10}$$

In the last equality, we have used the fact that ϕ, the volume fraction of the inclusions, equals to V_i/V.

The effective dielectric constant ε of the composite is defined by $\langle\vec{D}\rangle = \varepsilon\langle\vec{E}\rangle$. From Equations 9 and 10, we get

$$\begin{aligned}\varepsilon &= \varepsilon_m + \phi(\varepsilon_i - \varepsilon_m)\frac{\vec{E}_i}{\langle\vec{E}\rangle} \\ &= \varepsilon_m + \phi(\varepsilon_i - \varepsilon_m)\frac{\vec{E}_i}{\phi\vec{E}_i + (1-\phi)\vec{E}_m}\end{aligned} \tag{11}$$

Using Equation 8, we finally obtain

$$\varepsilon = \varepsilon_m + \phi(\varepsilon_i - \varepsilon_m)\frac{1}{\phi + (1-\phi)\frac{\varepsilon_i + 2\varepsilon_m - \phi(\varepsilon_i - \varepsilon_m)}{3\varepsilon_m}} \tag{12}$$

Note that when $\phi = 0$, Equation 12 gives $\varepsilon = \varepsilon_m$ and when $\phi = 1$, it yields $\varepsilon = \varepsilon_i$, as expected.

Equation 12 can also be written in the form:

$$\frac{\varepsilon}{\varepsilon_m} = 1 + \frac{\phi\left(\frac{\varepsilon_i}{\varepsilon_m} - 1\right)}{\phi + \frac{1}{3}(1-\phi)\left[\frac{\varepsilon_i}{\varepsilon_m}(1-\phi) + \phi + 2\right]} \tag{13}$$

Note that when $\varepsilon_i = \varepsilon_m$, we have $\varepsilon = \varepsilon_m$, as required.

Fig. 1 shows the logarithm of the ratio $\varepsilon/\varepsilon_m$ for $\phi = 0$ to 1 for values of $\varepsilon_i/\varepsilon_m$, ranging from 0.001 to 1000.

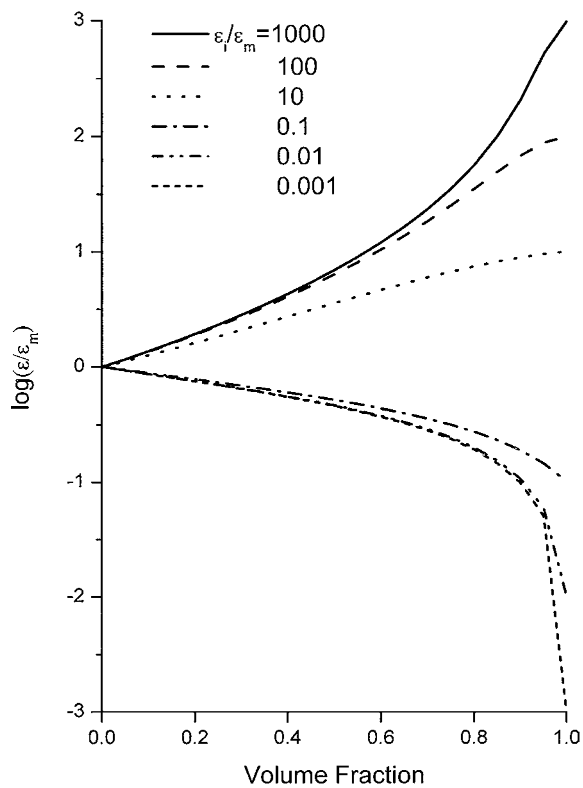


Figure 1 Logarithm of the relative effective dielectric constant values predicted by Equation 13 for various ratios of inclusion (ε_i) to matrix (ε_m) dielectric constants.

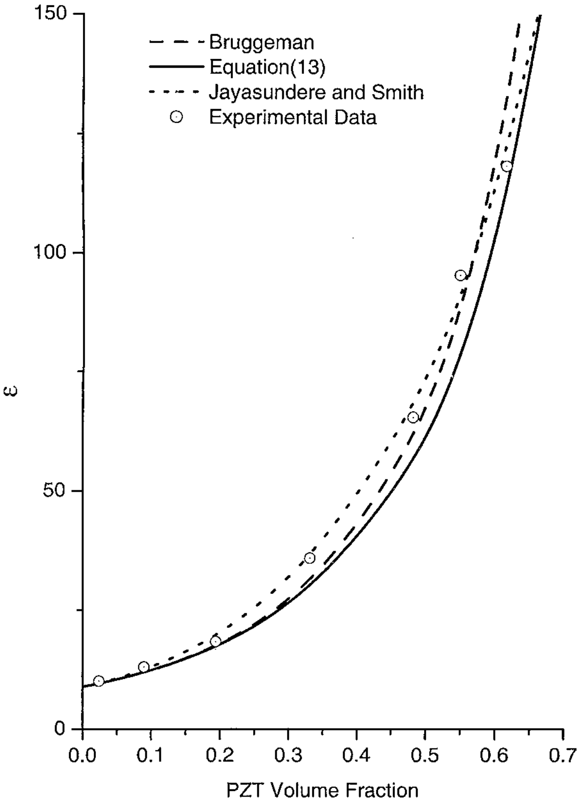


Figure 2 Predictions by Equation 13 compared with experimental data of Yamada [11], Bruggeman formula and the Jayasundere and Smith formula.

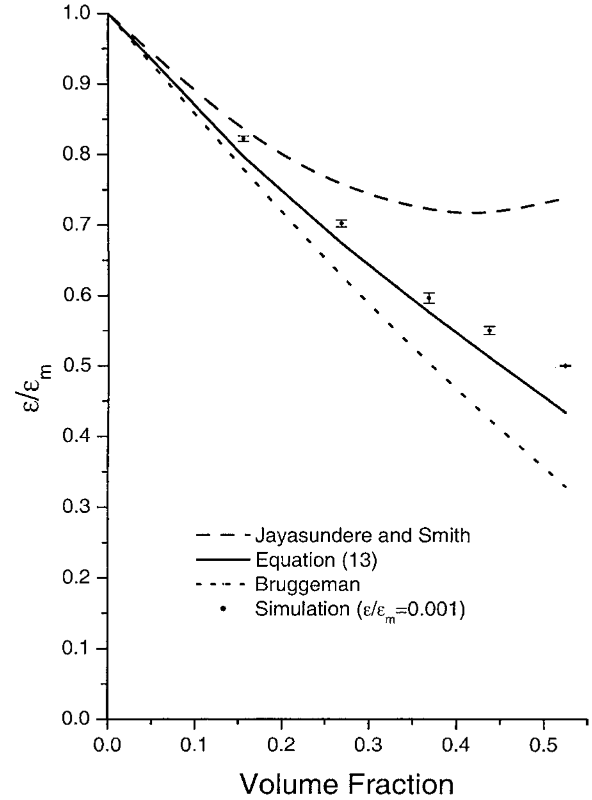


Figure 3 Predictions of Equation 13 compared with simulated data and the formulae due to Jayasundere and Smith, and Bruggeman.

When the inclusion volume fraction ϕ is sufficiently small, it can be shown that Equation 13, the Bruggeman formula and the Jayasundere and Smith formula all have the same form:

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

This is the well-known Maxell-Wagner formula [6], which is valid only for small ϕ values.

3. Comparison with experimental data ($\varepsilon_i > \varepsilon_m$ case)

Equation 13 is compared in Fig. 2 with the published experimental data of Yamada [11], which are dielectric constant values of a 0-3 system consisting of lead zirconate titanate (PZT) particles in a polyvinylidene fluoride (PVDF) matrix. In the same figure, we have also shown the predictions due to Bruggeman's formula and the Jayasundere-Smith fromula. While all formulae give reasonably good estimates of the experimental data, as we have pointed out in the Introduction, the Jayasundere's formulation suffers from not giving correct asymptotic internal electric field inside the inclusions when $\phi = 1$.

4. Comparison with simulated data ($\varepsilon_i < \varepsilon_m$ case)

When ε_i is less than ε_m, Equation 13 is still valid. Since it is difficult to find experimental data for this case, we have in the present study employed a boundary element simulation program to generate data for the effective dielectric constant. The program generates 64 spheres having dielectric constant $\varepsilon_i = 1$ embedded randomly (without overlapping) inside a cube of matrix material having dielectric constant ε_m. Two opposite sides of the cube are then considered to be equipotential surfaces with an electric potential difference U applied across them. The resulting total charge Q on each surface is then calculated and the effective dielectric constant ε of the composite is found by the formula $\varepsilon = Q/(UL)$, where L is the length of a side of the cube. With both the number of spheres and their radii kept constant, the value of L is varied to give different volume fractions of the spheres in the cube.

Fig. 3 shows the simulated data and those predicted by Equation 13, the equations due to Jayasundere and Smith, and Bruggeman. In this figure, for each volume fraction value, the simulated value shown is the average value found from five random spatial distributions of the spheres.

Obviously, the Jayasundere prediction is too deviated from the simulated data because as stated earlier, it is not applicable for this situation.

When compared with the Bruggeman formula, it is clear that Equation 13 gives a better fitting to the simulated values.

5. Effective complex permittivity

Consider a harmonically oscillating electric field with amplitude E_o and angular frequency ω applied across the composite. If both the inclusion and the matrix materials are non-conductive, in the quasi-static limit, the dielectric constant ε can be replaced by the complex permittivity ε^*, which is a function of ω, defined by $\varepsilon^*(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega)$.

Using Equation 13, we get

$$\begin{aligned}\varepsilon' = \frac{1}{F}\{&(C\varepsilon'_{\mathrm{m}} + D\varepsilon'_{\mathrm{i}})[\varepsilon'_{\mathrm{m}}(A\varepsilon'_{\mathrm{i}} + D\varepsilon'_{\mathrm{m}}) \\ &- \varepsilon''_{\mathrm{m}}(A\varepsilon''_{\mathrm{i}} + B\varepsilon''_{\mathrm{m}})] + (C\varepsilon''_{\mathrm{m}} + D\varepsilon''_{\mathrm{i}}) \\ &\times [\varepsilon''_{\mathrm{m}}(A\varepsilon'_{\mathrm{i}} + B\varepsilon'_{\mathrm{m}}) + \varepsilon'_{\mathrm{m}}(A\varepsilon''_{\mathrm{i}} + D\varepsilon''_{\mathrm{m}})]\} \quad (14)\end{aligned}$$

$$\begin{aligned}\varepsilon'' = \frac{1}{F}\{&(C\varepsilon'_{\mathrm{m}} + D\varepsilon'_{\mathrm{i}})[\varepsilon''_{\mathrm{m}}(A\varepsilon'_{\mathrm{i}} + D\varepsilon'_{\mathrm{m}}) \\ &+ \varepsilon'_{\mathrm{m}}(A\varepsilon''_{\mathrm{i}} + B\varepsilon''_{\mathrm{m}})] - (C\varepsilon''_{\mathrm{m}} + D\varepsilon''_{\mathrm{i}}) \\ &\times [\varepsilon'_{\mathrm{m}}(A\varepsilon'_{\mathrm{i}} + B\varepsilon'_{\mathrm{m}}) - \varepsilon''_{\mathrm{m}}(A\varepsilon''_{\mathrm{i}} + D\varepsilon''_{\mathrm{m}})]\} \quad (15)\end{aligned}$$

where A, B, C, D and F are defined by:

$$\begin{aligned}A &= \phi + (1-\phi)^2/3 \\ B &= (1-\phi)(2+\phi)/3 \\ C &= \phi + (1-\phi)(2+\phi)/3 \\ D &= (1-\phi)^2/3 \\ F &= (C\varepsilon'_{\mathrm{m}} + D\varepsilon'_{\mathrm{i}})^2 + (C\varepsilon''_{\mathrm{m}} + D\varepsilon''_{\mathrm{i}})^2\end{aligned}$$

Similarly, the Jayasundere and Smith formula gives the following effective complex permittivity:

$$\varepsilon' = \varepsilon'_{\mathrm{i}} - \frac{1-\phi}{M^2+N^2}[(\varepsilon'_{\mathrm{i}} - \varepsilon'_{\mathrm{m}})M + (\varepsilon''_{\mathrm{i}} - \varepsilon''_{\mathrm{m}})N] \quad (16)$$

$$\varepsilon'' = \varepsilon''_{\mathrm{i}} - \frac{1-\phi}{M^2+N^2}[(\varepsilon''_{\mathrm{i}} - \varepsilon''_{\mathrm{m}})M - (\varepsilon'_{\mathrm{i}} - \varepsilon'_{\mathrm{m}})N] \quad (17)$$

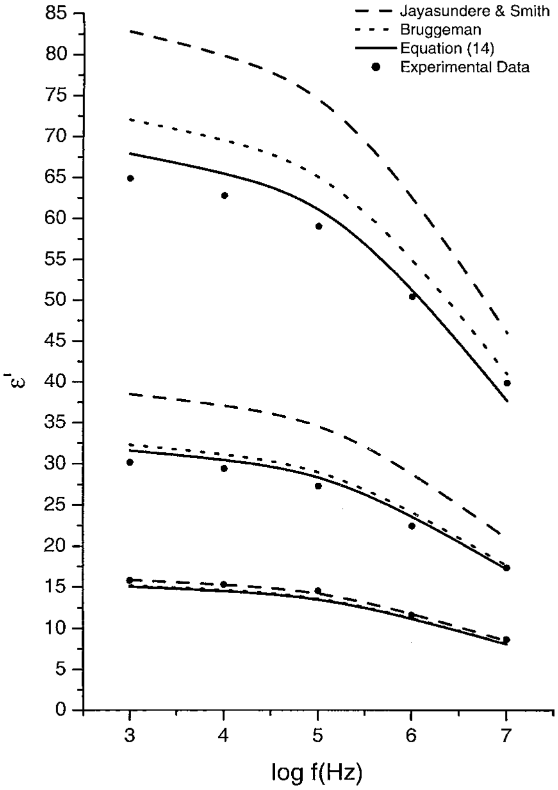
where

$$\begin{aligned}M &\equiv 1 - \phi + \frac{3\phi}{I^2+J^2}(IK + JL) \\ N &\equiv \frac{3\phi}{I^2+J^2}(IL - JK)\end{aligned}$$

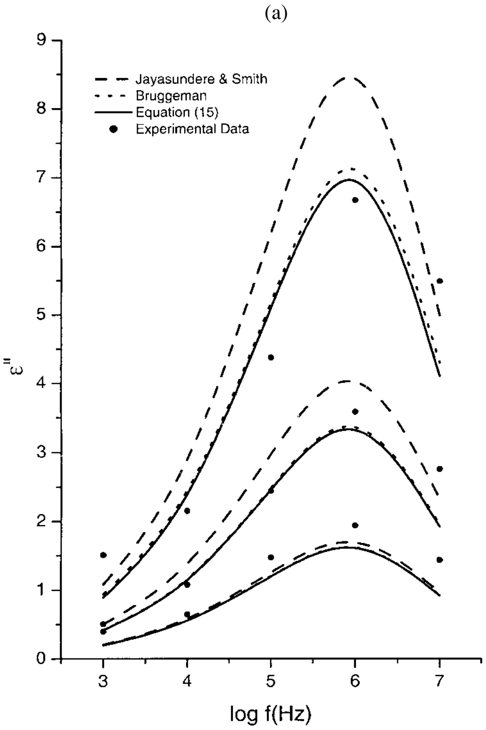
and

$$\begin{aligned}I &\equiv (\varepsilon'_{\mathrm{i}} + \varepsilon''_{\mathrm{i}} + 2\varepsilon'_{\mathrm{m}} + 2\varepsilon''_{\mathrm{m}})(\varepsilon'_{\mathrm{i}} - \varepsilon''_{\mathrm{i}} + 2\varepsilon'_{\mathrm{m}} - 2\varepsilon''_{\mathrm{m}}) \\ J &\equiv 2(\varepsilon'_{\mathrm{i}} + 2\varepsilon'_{\mathrm{m}})(\varepsilon''_{\mathrm{i}} + 2\varepsilon''_{\mathrm{m}}) \\ K &\equiv \varepsilon'_{\mathrm{m}}[(1+3\phi)\varepsilon'_{\mathrm{i}} + (2-3\phi)\varepsilon'_{\mathrm{m}}] \\ &\quad - \varepsilon''_{\mathrm{m}}[(1+3\phi)\varepsilon''_{\mathrm{i}} + (2-3\phi)\varepsilon''_{\mathrm{m}}] \\ L &\equiv \varepsilon''_{\mathrm{m}}[(1+3\phi)\varepsilon'_{\mathrm{i}} + (2-3\phi)\varepsilon'_{\mathrm{m}}] \\ &\quad + \varepsilon'_{\mathrm{m}}[(1+3\phi)\varepsilon''_{\mathrm{i}} + (2-3\phi)\varepsilon''_{\mathrm{m}}]\end{aligned}$$

Fig. 4a and b show, respectively, the values predicted by Equations 14 through 17, compared with experimental data for particulates of barium titanate ($BaTiO_3$) in a polyvinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) matrix [12].



(a)



(b)

Figure 4 (a) Real part of the effective complex permittivity predicted by Equation 14, compared with experimental data (circles) of Cheung *et al.* [12] and formulae due to Jayasundere and Smith (dashed lines), and Bruggeman (dotted lines). From top to bottom, the volume fractions of the inclusions are 0.49, 0.31 and 0.1, respectively. (b) Imaginary part of the effective complex permittivity predicted by Equation 14, compared with experimental data (circles) of Cheung *et al.* [12] and formulae due to Jayasundere and Smith (dashed lines), and Bruggeman (dotted lines.) From top to bottom, the volume fractions of the inclusions are 0.49, 0.31 and 0.1, respectively.

In our calculation, the experimental data for $BaTiO_3$ ceramic is taken from von Hippel [13]. Also shown are the values predicted by a linearized version of Bruggeman's formula [2, 3], reproduced below in our notation for completeness.

$$\frac{\varepsilon'_{\mathrm{i}} - \varepsilon'}{(\varepsilon')^{1/3}} = \frac{(1-\phi)(\varepsilon'_{\mathrm{i}} - \varepsilon'_{\mathrm{m}})}{(\varepsilon'_{\mathrm{m}})^{1/3}} \tag{18}$$

$$\varepsilon'' = \frac{(\varepsilon'_{\mathrm{i}} - \varepsilon')(\varepsilon'_{\mathrm{i}} + 2\varepsilon'_{\mathrm{m}})\varepsilon'\varepsilon''_{\mathrm{m}}}{(\varepsilon'_{\mathrm{i}} - \varepsilon'_{\mathrm{m}})(\varepsilon'_{\mathrm{i}} + 2\varepsilon')\varepsilon'_{\mathrm{m}}} + \frac{3(\varepsilon' - \varepsilon'_{\mathrm{m}})\varepsilon'\varepsilon''_{\mathrm{i}}}{(\varepsilon'_{\mathrm{i}} - \varepsilon'_{\mathrm{m}})(\varepsilon'_{\mathrm{i}} + 2\varepsilon')} \tag{19}$$

Again, note that ε' is still implicitly expressed in Equation 18 and ε'' depends on its value.

Fig. 4a and b depict that while at low inclusion volume fraction ($\phi = 0.1$), all three formulae predict values close to the experimental data; however, Equation 13 out-performs the others when the volume fraction is high ($\phi = 0.49$).

6. Conclusion

The main idea involved in our derivation is to consider the displacement field as experienced by a single particulate as the sum of two parts: one due to the pure medium and the other due to the polarization of the particulates embedded in the medium. By doing so, the interaction between the particulates is taken into account. This idea is verified when compared with experimental data, for we have shown, in Section 5, that the derived formulae give reasonably good estimation for the effective dielectric constant for inclusion volume fraction up to about 0.5.

To conclude, we have derived a simple, analytical formula for the prediction of the effective dielectric constant of binary 0-3 composite materials. For non-conductive constituents, it also predicts the effective complex permittivity. Compared with the Jayasundere and Smith formula, it gives the correct asymptotic value for the internal electric field of the inclusions when their volume fraction approaches one. It is applicable for a larger range of the volume fraction of the inclusions and is valid for all values for the dielectric constants of the constituents, especially, for case $\varepsilon_{\mathrm{i}} < \varepsilon_{\mathrm{m}}$. Compared with Bruggeman's formula, it fits better to the simulated data for the case $\varepsilon_{\mathrm{i}} < \varepsilon_{\mathrm{m}}$ and the fact that it is an explicit formula for the effective value makes it more convenient to use, especially when the value is to be embedded into another formula.

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