Applicability Study of Classical and Contemporary Models for Effective Complex Permittivity of Metal Powders

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ABSTRACT
Microwave thermal processing of metal powders has recently been a topic of a substantial interest; however, experimental data on the physical properties of mixtures involving metal particles are often unavailable. In this paper, we perform a systematic analysis of classical and contemporary models of complex permittivity of mixtures and discuss the use of these models for determining effective permittivity of dielectric matrices with metal inclusions. Results from various mixture and core-shell mixture models are compared to experimental data for a titanium/stearic acid mixture and a boron nitride/graphite mixture (both obtained through the original measurements), and for a tungsten/Teflon mixture (from literature). We find that for certain experiments, the average error in determining the effective complex permittivity using Lichtenecker’s, Maxwell Garnett’s, Bruggeman’s, Buchelnikov’s, and Ignatenko’s models is about 10%. This suggests that, for multiphysics computer models describing the processing of metal powder in the full temperature range, input data on effective complex permittivity obtained from direct measurement has, up to now, no substitute.

KEYWORDS: Core-shell model, effective complex permittivity, metal powder, mixture model, percolation threshold, perturbation technique.

INTRODUCTION
Microwave (MW) thermal processing of materials is gaining increasingly more attention as a promising interdisciplinary technology for volumetric heating with a potential for substantial energy savings. As a multiphysics phenomenon, MW heating is known to be complex and difficult to control. It has recently become evident that computer modeling could help clarify many issues involving interaction of microwaves with materials and could suggest engineering solutions for designing efficient MW systems. Major progress has been made due to the development of computational schemes based on implementation of coupled electromagnetic-thermal models (e.g. [Mishra et al., 2006; Duan et al., 2006; Celuch et al., 2006; Al-Rizzo et al., 2007a; Al-Rizzo et al., 2007b; Kopyt and Celuch, 2007; Sabliov et al., 2007; Tilford et al., 2007, Watanabe et al., 2010; Zhu et al., 2007a; Zhu et al., 2007b; Sun et al., 2009a; Celuch
and Kopyt, 2009; Salvi et al., 2010; Yakovlev et al., 2011). Recently, attempts to couple electromagnetic and thermal solvers with tools for modeling associated mechanical deformation have been also reported as initial steps toward the development of a comprehensive macroscopic modeling technique for MW sintering [Demjanenko et al., 2010; Bogachev et al., 2011]. However, regardless of the level of accuracy of the numerical techniques and the degree of idealization applied, the adequacy of the model depends to a great extent on the quality of input data on material parameters. This study is motivated by the strong need for data on electromagnetic parameters for use in multiphysics modeling of MW processing of materials. This need has recently become even more acute upon the discovery of the applicability of microwave energy in processing metal powders [Roy et al., 1999]. While the techniques of measuring complex permittivity of dielectric materials are well developed, and experimental data on the dielectric constant and loss factors are widely available for a vast range of dielectrics, quite often the effective complex permittivity of metal powders are not present in the literature, and even when they are, conflicting values (sometimes up to orders of magnitude) can be found [Bouvard et al., 2010]. This paper aims to summarize and draw more attention to the potential practical applications of some classical and contemporary mathematical models for determining permittivity of composites and mixtures that might be applicable to metal powders. We briefly review the most notable models, present them in closed form, examine the ranges of validity of their input parameters, and discuss their practical applicability with reference to our original measurements of effective complex permittivities of mixtures of titanium and stearic acid, and of graphite and boron nitride, and to the results by Zimmerman et al. [Zimmerman et al., 2008] in determining the loss factor of a tungsten/Teflon mixture. We discuss the reasons for discrepancies between the results obtained from the models and the experiments. Under the identified limitations for their use, all of the models we consider, i.e. the classical mixture models by Lichtenecker, Maxwell Garnett, and Bruggeman and the contemporary core-shell mixture models by Buchelnikov [Buchelnikov et al., 2008a; Buchelnikov et al., 2008b] and Ignatenko [Ignatenko et al., 2009; Ignatenko and Tanaka, 2010] are shown to be operational and provide, for certain experiments, about 10% average error in determining the effective complex permittivity of powders in which the volume fraction of metal is below the percolation threshold.

REVIEW OF THE MODELS

Lichtenecker’s Logarithmic Mixture Formula

Lichtenecker’s logarithmic mixture formula [Lichtenecker, 1926; Lichtenecker and Rother, 1931] can be used to compute the permittivity most efficiently as follows:

$$
\varepsilon_{\text{eff}} = \prod_{n=1}^{N} \varepsilon_n^{\alpha_n},
$$

where the $i^{\text{th}}$ component of the $N$ substances comprising the mixture is said to have effective permittivity $\varepsilon_{i}$ and volume fraction $\alpha_{i}$. When this model is used for estimating $\varepsilon_{\text{eff}} = \varepsilon' - j\varepsilon''$ of a mixture in which the $i^{\text{th}}$ component is a metal powder, then $\varepsilon_{i}$ should represent the effective conductivity of the metal powder in air.

The formula has been used recently to calculate effective complex permittivity of various mixtures of dielectric substances such as silica and ferrite powders [Ebara et al., 2006], pavement mixtures [Shafri et al., 2008], polyelectric sensors [Olszowy, 2003], and biological cells [Saito et al., 2008]. Some recent efforts have been focused on developing a physical foundation for the original Lichtenecker mixture formula, including a study [Zakri et al., 1998] that assumes a beta distribution of inclusion...
shapes and uses effective medium theory to physically motivate the formula. A more recent paper [Goncharenko et al., 2000] analyzed the formula in the context of spectral representation, attempting to characterize the range of anisotropic systems to which it is applicable. In particular, they showed that the Lichtenecker formula has a wider area of applicability than Bruggeman’s formula or the Maxwell Garnett equations. Recently, Simpkin showed that the Lichtenecker formula may be of a still more fundamental nature, by deriving the formula directly from Maxwell’s equations and the principle of charge conservation under the assumption of a random spatial distribution of shapes and orientations of inclusions in a dielectric mixture [Simpkin, 2010]. This characterization indicates that the closer the spatial distribution of components is to being random, the more accurate will be Lichtenecker’s approximation of effective permittivity, which may account for the errors noted in previous work. Simpkin also showed how the Maxwell Garnett equations are derived from Lichtenecker’s equations under certain conditions.

Reynolds and Hough [Reynolds and Hough, 1957] asserted that the theoretical justification of the original Lichtenecker formulas [Lichtenecker, 1931] was based on the incorrect assumption that the final dielectric constant of a mixture is independent of the method of preparation of the mixture. In particular, they cited two assumptions made in the derivation of the formula, which they claimed can hold simultaneously neither in the case when particles of two materials are formed during two-stage mixing, nor in the case when particles are not formed. This assertion was reinforced in [Dukhin and Shilov, 1974], where the authors showed that this statement resulted from the erroneous consideration of a disperse system as simultaneously both ordered and chaotic. In 1985, Neelakantaswamy et al. [Neelakantaswamy et al., 1985] proposed corrections to the Lichtenecker mixture formula to address these concerns by considering $\varepsilon_{\text{eff}}$ not as a logarithmic mean, but differently as a form of weighted geometric mean. The final formulation they present for a mixture of two substances is as follows:

$$
\varepsilon_{\text{eff}} = \begin{cases} 
\frac{X(\alpha)}{2}, & \varepsilon_1 > \varepsilon_2, 0 \leq \alpha \leq \alpha_1 \\
\frac{Y(\alpha)}{2}, & \varepsilon_1 < \varepsilon_2 \\
\frac{1}{2} \left[ \frac{1}{2C(\alpha_1)} + \frac{1}{2C(\alpha_2)} \right] C(\alpha)Z(\alpha), & \varepsilon_1 > \varepsilon_2, \alpha_1 \leq \alpha \leq \alpha_2 \\
\frac{1}{2} \left[ \frac{1}{2C(\alpha_1)} + \frac{1}{2C(\alpha_2)} \right] C(\alpha)Z(\alpha), & \varepsilon_1 < \varepsilon_2 \\
\frac{Y(\alpha)}{2}, & \varepsilon_1 > \varepsilon_2, \alpha_2 \leq \alpha \leq 1 \\
\frac{Y(\alpha)}{2}, & \varepsilon_1 < \varepsilon_2
\end{cases}
$$

where

$$
X(\alpha) = Z(\alpha) + \frac{1}{\varepsilon_L},
$$

$$
Y(\alpha) = Z(\alpha) + \varepsilon_U,
$$

$$
Z(\alpha) = \frac{\varepsilon_U^n}{\varepsilon_L^{n-1}},
$$

$$
A(\alpha) = 1 + \frac{1}{\varepsilon_U^n \varepsilon_L^{n-1}},
$$

$$
B(\alpha) = 1 + \frac{1}{\varepsilon_U^{n-1} \varepsilon_L^n},
$$

$$
C(\alpha) = \sqrt[1-\alpha]{\frac{\varepsilon_U}{\varepsilon_L} \varepsilon_1^{\alpha} \varepsilon_2^{1-\alpha}}.
$$

Here, $\varepsilon_U$ and $\varepsilon_L$ denote Wiener’s upper and lower limits, respectively. This formulation is based on results in [Kidnasamy and Neelakantaswamy, 1984] with estimates related to eccentricity of ellipsoidal inclusions taken from Coelho [Coelho, 1979], and is valid only when

$$
\frac{\varepsilon_1 \varepsilon_2}{(\varepsilon_1 - \varepsilon_2)^2} - \frac{\varepsilon_1 + \varepsilon_2}{2(\varepsilon_1 - \varepsilon_2) \ln \left[ \frac{\varepsilon_1}{\varepsilon_2} \right]} \geq \frac{1}{4}.
$$
in order for Wiener’s upper and lower limits to be positive.

The dependence of this formula on eccentricity, unlike the original Lichtenecker formula, takes into account the shape of the inclusions; Neelakanteswamy’s correction can thus be considered an extension, as well as a correction, of Lichtenecker’s formula.

Maxwell Garnett Mixing Rule

First presented in [Maxwell Garnett, 1904; Maxwell Garnett, 1905], the two-phase Maxwell Garnett formula was developed to determine the optical properties of a particular glass substance that contained minute spherical particles of gold, and as such, is suitable to describe mixtures involving metal particles, provided that those mixtures satisfy validity conditions discussed below. The formulation for a mixture of two materials is as follows:

\[ \varepsilon_{\text{eff}} = \varepsilon_1 \left[ \frac{\varepsilon_2 (1 + 2\alpha) - \varepsilon_1 (2\alpha - 2)}{\varepsilon_1 (2 + \alpha) + \varepsilon_2 (1 - \alpha)} \right] \]

where \( \alpha \) is the volume ratio of the embedded material, \( \varepsilon_2 \) is the permittivity of the embedded material, and \( \varepsilon_1 \) is the permittivity of the matrix material. Simpkin has shown that, under the condition that the value \( 2\alpha\varepsilon_2 - \varepsilon_1\varepsilon_2 + 2\varepsilon_1 \) is small, the Maxwell Garnett equations may be derived as an approximation to Lichtenecker’s formula [Simpkin, 2010].

In general, the Maxwell Garnett model is valid for mixtures that are electrodynamically isotropic, with parameters that do not depend on the intensity of the electric field and do not change in time, with inclusions that are small compared to the wavelength and are separated by distances greater than their size, and with inclusions, if they are of a conductive material, at a concentration lower than the percolation threshold [Koledintseva et al., 2006].

Since its original formulation, the model has been used to calculate permittivity of various mixtures, including those of glass spheres, quartz sand grains [Robinson and Friedman, 2002], and snow [Sihvola et al., 1985].

In 1984, Thériault and Boivin revised the Maxwell Garnett theory to include the shape factor and size of metal particles suspended in a dielectric matrix, and observed good agreement with reality for volume fractions ranging from 0 to 0.12 [Thériault and Boivin, 1984]. Their formula for \( \varepsilon_{\text{eff}} \) is as follows:

\[ \frac{\varepsilon_{\text{eff}} - \varepsilon_m}{s\varepsilon_{\text{eff}} + (1-s)\varepsilon_m} = \alpha \frac{\varepsilon_i - \varepsilon_m}{s\varepsilon_i + (1-s)\varepsilon_m} \]

where \( \varepsilon_m \) is the permittivity of the matrix, \( \varepsilon_i \) is the permittivity of the inclusion, \( \alpha \) is the volume fraction of the inclusions, and \( s \) is the shape factor of the metal particles, given below as a function of \( \varepsilon_{\text{eff}} \):

\[ s = \frac{\alpha \varepsilon_i (R) - \varepsilon_{\text{eff}} + (1-\alpha)\varepsilon_m}{(1-\alpha)(\varepsilon_{\text{eff}} - \varepsilon_m)(\varepsilon_i (R) - \varepsilon_m)} \]

where \( R \) is the radius of the inclusions.

A Maxwell Garnett type model also exists to account for arbitrarily many types of inclusions (which may be metal) in a dielectric matrix, and was used recently to describe the properties of microwave absorbing materials containing an arbitrary number of different types of carbon particles [Koledintseva et al., 2006]. The formula is as follows:

\[ \varepsilon_{\text{eff}} = \varepsilon_m + \frac{1}{3} \sum_{i=1}^{n} \alpha_i (\varepsilon_i - \varepsilon_m) \sum_{k=1}^{3} \frac{\varepsilon_m}{\varepsilon_m + N_k \varepsilon_m} \]

where \( \varepsilon_m \) is the relative permittivity of the matrix dielectric, \( \varepsilon_i \) is the permittivity and \( \alpha_i \) is the volume fraction occupied by the \( i^{th} \) type of inclusion, and \( N_k \) are the depolarization factors of the \( i^{th} \) type of inclusion; \( k = 1, 2, 3 \) corresponds to \( (x, y, z) \) in Cartesian coordinates.
Bruggeman’s Symmetric Mixture Formula

Bruggeman’s symmetric mixture formula for a two-part mixture, introduced in [Bruggeman, 1935], is:

\[
\alpha \left( \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}} \right) + (1 - \alpha) \left( \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 + 2\varepsilon_{\text{eff}}} \right) = 0,
\]

where \(\alpha\) is the volume fraction, and the components have permittivities \(\varepsilon_1\) and \(\varepsilon_2\) respectively.

The Bruggeman mixture formula was considered in [Reynolds and Hough, 1957] to be an extension of Lichtenecker’s formulas to the more complicated cases of mixtures that could be anisotropic. Simpkin showed that Bruggeman’s formula results from the classical Lichtenecker formula, under the assumption that the factors \(F_1\) and \(F_2\),

\[
F_1 = \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}}, \quad F_2 = \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 + 2\varepsilon_{\text{eff}}}
\]

are small enough in magnitude for the dependence of Lichtenecker’s formula on them to be taken as linear, which is equivalent to considering only first-order interactions between each component of the mixture embedded in a homogeneous effective medium [Simpkin, 2010].

Bruggeman’s formula is quadratic in \(\varepsilon_{\text{eff}}\), and always has a positive discriminant together with a strictly negative root; in order to be a solution, the other root must be positive, which motivates the restriction that

\[
\varepsilon_i (2 - 3 \alpha) \leq \varepsilon_1 (1 - 3 \alpha) + \sqrt{(\varepsilon_1 (2 - 3 \alpha) + \varepsilon_2 (3 \alpha - 1))^2 + 8 \varepsilon_2 \varepsilon_2}.
\]

The results produced by Bruggeman’s formula should be verified, i.e., it should be determined that this restriction is, in fact, satisfied. If not, then a different model should be used.

Ignatenko’s Extension for Compacted Metal Powders

Ignatenko et al. [Ignatenko et al., 2009; Ignatenko and Tanaka, 2010] give Bruggeman’s formula differently for compacted mixtures involving core-shell metal particles. This model is developed specifically for metal powders, and to this end takes into account the oxide layer that forms on particles of metal, resulting in core-shell type particles of the kind shown in Figure 1.

The central formula of the model is as follows:

\[
\alpha \left( \frac{\varepsilon_p - \varepsilon_{\text{eff}}}{\varepsilon_p + 2\varepsilon_{\text{eff}}} \right) + (1 - \alpha) \left( \frac{\varepsilon_g - \varepsilon_{\text{eff}}}{\varepsilon_g + 2\varepsilon_{\text{eff}}} \right) = 0
\]

where \(\alpha\) is the volume fraction of the particles, \(\varepsilon_g\) is the permittivity of gas in pores, and \(\varepsilon_p = \varepsilon_2 G_2\), with the coefficient \(G_2\) defined as:

\[
G_2 = \frac{1}{2} \frac{R_1^3}{R_2} G_1, \quad G_1 = \frac{1 - \left( \frac{\varepsilon_1}{\varepsilon_2} \right)^3}{1 + 2 \left( \frac{R_1}{R_2} \right)^3 G_1}, \quad G_0 = \frac{1}{2} \frac{\varepsilon_1}{\varepsilon_2} \frac{y \cos y + \sin y}{\varepsilon \cos y - \sin y + y^2 \sin y}
\]

where \(R_{1,2}\) are the radii and \(\varepsilon_{1,2}\) are the permittivity values of the core and shell, respectively. The argument of the factor \(G_0\) is \(y = k_1 R_1\), where \(k_1 = \omega (\varepsilon \mu / \mu_1)^{1/2}\), \(\mu_1\) is the permeability, \(\omega = 2\pi f\), and \(f\) is the frequency of the electromagnetic wave irradiating
the sample. The skin depth of highly conductive non-magnetic core material can be accounted for by setting $y = (1 + i)R_1/\delta$, where $\delta$ is the skin depth.

**Buchelnikov’s Model for Core-Shell Powders**

Like the above model by Ignatenko, the model presented by Buchelnikov et al. [Buchelnikov et al., 2008a; Buchelnikov et al., 2008b] considers spherical core-shell particles randomly distributed in the effective medium. The authors determine the following relationship between the effective permittivity of the mixture and the radii of the spherical inclusions:

$$\epsilon_{\text{eff}} = \left( \frac{3\epsilon_1 + (\zeta - 1)(\epsilon_1 + 2\epsilon_2)}{2a\epsilon_{\text{eff}} + b\epsilon_2} \right) + \frac{(1 - \alpha\zeta)\epsilon_g - \epsilon_{\text{eff}}}{\epsilon_g + \epsilon_{\text{eff}}} = 0$$

where $\alpha$ is the volume fraction of the metal inclusions, $\epsilon_g$ is the permittivity of the gas or vacuum, $\epsilon_{1,2}$ are the permittivities of the metallic core and shell respectively, and the expressions for $\zeta$, $a$, and $b$ are:

$$\zeta = \left( \frac{R_2}{R_1} \right)^3 = (1 + l)^3$$

$$l = \frac{R_2 - R_1}{R_1}$$

$$a = (\zeta - 1)\epsilon_1 + (2\zeta + 1)\epsilon_2$$

$$b = (2 + \zeta)\epsilon_1 + 2(\zeta - 1)\epsilon_2$$

where $R_{1,2}$ are the radii of the metallic core and shell respectively. In the limiting cases $R_1 \rightarrow 0$ and $R_2 \rightarrow R_1$, Buchelnikov’s model reduces to exactly the Bruggeman equations.

**EXPERIMENTAL STUDIES**

In this section, we describe three experimental attempts to evaluate the effective complex permittivity of mixtures involving metal powders at 2.45 GHz. The three sets of results are obtained for different types of metal powders, and thus provide a diverse set of material for testing the performance of the described models.

**Tungsten/Teflon Mixture**

In [Zimmerman et al., 2008], the authors determined experimentally the effective complex permittivity of mixtures of tungsten and Teflon powders. They made samples with varying volume fractions of tungsten, formed the mixtures into cylindrical pellets (of diameter 41 mm and height 64 mm) with varying particle sizes, and determined $\epsilon'$ and $\tan \delta = \epsilon''/\epsilon'$ of each sample using cavity perturbation techniques.

**Titanium/Stearic Acid Mixture**

In our own experiment, we mechanically mixed gas atomized titanium particles (spherical, 25 microns, Pyrogenesis Canada, Inc.) with stearic acid (Sigma-Aldrich Co., 95%) in various volume fractions. These mixtures were compacted uniaxially into cylindrical pellets of diameter 10 mm and height 20 mm.

**Hexagonal Boron Nitride/Graphite Mixture**

Graphite particles (flakes, 4 microns, TIMCAL Ltd.) and hexagonal boron nitride powder (10 microns, Kennametal Sintec Keramik GmbH) were mixed in an agate mortar in various volume fractions and pressed uniaxially to from cylindrical samples of 10 mm in diameter and 20 mm in height.

**Effective Permittivity Measurement**

The effective complex permittivity was determined based on a cavity perturbation approach [Waldron et al. 1960; Li et al. 1981; Meng et al. 1995] where the transverse magnetic mode $TM_{010}$ of a cylindrical resonator with two coaxial holes is used. The cavity perturbation formalism was assumed valid, and was applied to extract the effective complex permittivity from the frequency shift and the quality factor.
The cylindrical samples, longer than the cavity height, were inserted coaxially and maintained in center of the cavity. The variations of resonant frequency of the cavity as well as its quality factor due to the presence of the sample were determined with an HP 8720D Network Analyzer. As the numerical methods can present large uncertainties for high permittivity, the complex permittivity of the sample was evaluated using a calibration method based on standard samples.

MODELS VERSUS EXPERIMENTS

Input Data

The experiments mentioned in the previous Section were used for testing the results produced by the mixture and core-shell mixture models reviewed above. In computations for the tungsten/Teflon mixture, the effective complex permittivity of pure tungsten was taken as $30.0 + j8.0$ [Veronesi et al., 2003], for Teflon, the complex permittivity was assumed to be $2.29 + j0.03$ [Eves et al., 2008]. Values used for the effective complex permittivity of titanium and the stearic acid were taken directly from our experiment, and they were $10.55 + j1.0$ and $3.95 + j0.006$, respectively. The permittivity of the oxide layer was picked, in accordance with [Tobar et al., 1998], as $114 + j0.003$. The conductivity of titanium was taken to be $4.2 \times 10^9$ S/m, in accordance with [Reuben, 1998].

Our experiment was also the source of data on the effective complex permittivity of graphite ($25.5 + j0.15$) and of boron nitride ($3.05 + j0.006$). The conductivity of boron nitride was estimated at $1.0 \times 10^9$ S/m following the data of [Nose et al., 2006].

Mixture Models

The effective complex permittivities of all three mixtures were computed for different volume fractions ($\alpha$) using the Lichtenecker, Maxwell Garnett, and Bruggeman mixture models and plotted on the same graphs as the experimental results (Figures 2-4).

The experimentally determined material properties of all materials exhibit distinct percolation behaviors, characterized by a peak in the loss factor at volume fractions that depend on the average particle size of the mixtures. It is seen from the graphs that none of the mixture models were capable of predicting this percolation behavior. However, for low values of $\alpha$, the
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Table I. Errors in determining the effective complex permittivity of dielectric matrices with metal inclusions by the mixture models below percolation threshold.

<table>
<thead>
<tr>
<th>Model Mixture</th>
<th>Quantity</th>
<th>Lichtenecker</th>
<th>Maxwell Garnett</th>
<th>Bruggeman</th>
<th>Buchelnikov</th>
<th>Ignatenko</th>
</tr>
</thead>
<tbody>
<tr>
<td>titanium/stearic acid</td>
<td>$\varepsilon'$</td>
<td>8.0 %</td>
<td>14.0 %</td>
<td>10.7 %</td>
<td>10.9 %</td>
<td>6.5 %</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon''$</td>
<td>11.1 %</td>
<td>8.4 %</td>
<td>9.0 %</td>
<td>8.5 %</td>
<td>10.9 %</td>
</tr>
<tr>
<td>graphite/boron nitride</td>
<td>$\varepsilon'$</td>
<td>3.4 %</td>
<td>17.2 %</td>
<td>3.8 %</td>
<td>12.2 %</td>
<td>6.9 %</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon''$</td>
<td>above 20 %</td>
<td>above 20 %</td>
<td>above 20 %</td>
<td>above 20 %</td>
<td>above 20 %</td>
</tr>
</tbody>
</table>

Figure 3. Effective complex permittivity; dielectric constant (left) and the loss factor (right) of titanium/stearic acid mixture.

Figure 4. Effective complex permittivity; dielectric constant (left) and the loss factor (right) of graphite/boron nitride mixture.
measured and calculated data are quite close for certain experiments (Table I).

The error values were measured as the maximum deviation of the calculated values from the experimentally obtained values relative to the experimentally obtained values, taken before the percolation threshold for each material (the first four data points for titanium/stearic acid, and the first two points for graphite/boron nitride). The calculated errors seem to reveal that the Lichtenecker and Bruggeman models are more accurate in determining the real part of effective complex permittivity, while the Maxwell Garnett models produce lower error for the imaginary part.

**Core-Shell Model**

The effective complex permittivity of the titanium/stearic acid mixture was also calculated using Buchelnikov’s model and Ignatenko’s model on the core-shell particles; the results were plotted along with the experimental data in Figure 3.

Buchelnikov’s and Ignatenko’s formulas were also used here as three-phase mixture models to account directly for the presence of air ($\varepsilon_g = 1 + j0$) in the graphite/boron nitride mixture where the shape of conducting particles (graphite) is rather different from spheres assumed in the model. We take this fact into account through the following physical interpretation: after choosing a constant value for the “radius” of the particle that includes the graphite “core” and boron nitride “shell”, the number of particles in the mixture was determined for each set of volume fractions of graphite and boron nitride; subsequently, the thickness of the shell was calculated given the volume fraction of boron nitride. The two radii and three complex permittivity values (for graphite, boron nitride, and air) were used as inputs to Buchelnikov’s and Ignatenko’s models. Corresponding curves for $\varepsilon'$ and $\varepsilon''$ are shown in Figure 4.

It can be seen from the graphs that both of the core-shell models, when used to calculate the effective complex permittivity of the considered two mixtures, also do not predict percolation behavior. Table I therefore contains the errors characterizing the performance of this model for the volume fractions below percolation threshold; it is seen that, similar to other considered mixture models, these ones produce, for certain experiments, values of effective complex permittivity reasonably close to the experimental data.

**DISCUSSION**

Assuming that $\varepsilon'$ and $\varepsilon''$ are smooth functions of $\alpha$, a peak in $\tan \delta$ may occur only at those critical volume fractions $\alpha_p$ for which the first derivative of $\tan \delta$ is zero, that is:

$$\varepsilon''(\alpha_p) \frac{d\varepsilon'(\alpha_p)}{d\alpha} = \varepsilon'(\alpha_p) \frac{d\varepsilon''(\alpha_p)}{d\alpha}.$$  

Using the expression for complex permittivity predicted by Lichtenecker’s model, this situation occurs independently of volume fraction when $\varepsilon_1' \varepsilon_2' = \varepsilon_1'' \varepsilon_2''$, and in this case, all subsequent derivatives of $\tan \delta$ are zero, so no peak occurs for any mixture whose permittivity is treated by the Lichtenecker model. Using the expression for complex permittivity predicted by the Maxwell Garnett model, no zeros of the first derivative of $\tan \delta$ may exist for any mixture—so neither of these models are mathematically capable of predicting percolation behavior.

When compared with the measured values of $\varepsilon'$ and $\varepsilon''$ of two considered dielectric matrices with metal inclusions, the average error in determining the effective complex permittivity by all five models appears to be about 10%. Worse agreement with the measured values of $\varepsilon''$ of the graphite/boron nitride mixture may be conditioned also by a lower precision in the perturbation technique used for measurement of the loss factor of this low-loss mixture.

It should be noted that the multi-phase representations of Lichtenecker’s model and the Maxwell Garnett model could be used to more accurately account for
the volume fraction of air in compressed compact samples. In this case, air should be considered as a component of the mixture, together with the dielectric and metal powders involved, and its permittivity should be introduced as an input parameter. This consideration can be recommended as a possible extension of the two-phase approach studied in this paper. Another way of further developing the discussed modeling approach may be associated with generalization of the mixture-type formulas in the context of Weiner limits and Hashin-Shtrikman bounds [Sihvola, 2000].

CONCLUSION

This paper has presented and discussed various models, of both the mixture type and the core-shell type, for determining the effective complex permittivity of inhomogeneous media. We have tested some of these models against experimentally measured effective complex permittivity of mixtures of metal particles with dielectrics, namely, of tungsten/Teflon, titanium/stearic acid, and boron nitride/graphite, and have shown that none of the models of Lichtenecker, Bruggeman, Maxwell Garnett, Buchelnikov, and Ignatenko correctly predict behavior beyond the percolation threshold, but below it, they each do an acceptable job of quantitatively predicting the effective complex permittivity of the considered mixtures. Indeed, the continuum approximation that is valid for dielectric mixtures is applicable only below the percolation threshold of the conductive phase. Some disagreement with the experimentally calculated values may also arise from the lessened validity of the cavity perturbation formalism for volume fractions above the percolation threshold. The correction to Lichtenecker’s formula by Neelakantaswamy was not verified against experimental results in this study, because it relies on a characterization of inclusions as ellipsoidal, and this is not applicable to the experiments we have conducted.

REFERENCES


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