CHAPTER 6

Composite Dielectric Materials with a Discrete Conducting Phase

6.1 Introduction

A class of composite dielectric materials refers to a two-phase, host-inclusion system in which the inclusion is a discrete-phase of conducting medium (such as metals, semiconductors, or solid electrolytes) dispersed randomly or textured as an orderly embedment in the host medium which forms a dielectric receptacle. Such composites are essentially dielectric-conductor mixtures and have unique (effective) dielectic properties due to the fact that the constituent phases have extremely opposite characteristics as regards their electrical susceptance and the associated conduction phenomena. In view of the high electrical conductivity of the inclusions and predominant dielectric susceptance (lossy or lossless) of the host medium, prediction of effective dielectric permittivity and/or the conductivity of the composite medium is not simple or trivial.

Since the time of Maxwell-Garnett [1,2] attempts have been made, however, to evaluate the effective electrical characteristics of such conductor-insulator mixture systems. The primary factors which decide the effective parameters of such mixtures are: (i) Conductivity or complex permittivity of the inclusions; (ii) complex permittivity of the host medium; (iii) shape of the particulate inclusions; (iv) frequency; and (v) spatial arrangment (random or textured) of the inclusions in the receptacle.

In modeling conductor-insulator mixtures, two basic approaches have been pursued in general: One involves the treatment of the dielectric behavior of the mixtures entirely independent of the conductive effects of the inclusions and the other uses the expressions for complex dielectric properties of dielectric-dielectric mixtures with the conductive phase being treated as an extremely high-loss dielectric. In the second case, the mixture theories concerning dielectric-dielectric mixtures have been generalized to high-loss materials to account for the conductor inclusions; and the complex permittivity of the mixture is calculated with the surmise that the permittivity of the conductor inclusions approaches infinity. Thus, a mathematical way of decoupling dielectric considerations from the conductive phenomenon was formalized; and, in most cases, it appears that only the static (d.c.) or quasistatic (low frequency) behavior of such dielectric-conductor mixtures has been investigated to deduce the (lossless) static permittivity ε_S and/or the d.c conductivity σ_{dc} of the mixture. Pertinent to these existing models details on the evolution of background concepts are presented in the next section.

6.2 Evolution of Dielectric-Conductor Mixture Formulations

6.2.1 *Maxwell and Maxwell-Garnett formula*

Maxwell-Garnett [1,2] used the quasistatic (potential) approach to elucidate the effective (complex) permittivity $\hat{\sigma}_{eff}$ of the medium containing a volume loading θ of identical spherical particles of complex conductivity $\hat{\sigma}_2$ dispersed randomly in a homogeneous dielectric host medium of complex conductivity $\hat{\sigma}_1$. (Here, the complex conductivity $\hat{\sigma}$ is defined as $(\sigma + j\omega\varepsilon)$, ε being the permittivity and $\omega = 2\pi \times$ frequency.) The effective conductivity is then given by:

$$\hat{\sigma}_{eff} = \hat{\sigma}_2 (1 + 2\,\theta \mathcal{M}_o)/(1 - \theta \mathcal{M}_o) \tag{6.1}$$

where $\mathcal{M}_o$ is referred to as the normalized dipole moment. It has been deduced as [3]:

$$\mathcal{M}_o = (1 - \hat{\sigma}_1/\hat{\sigma}_2)(1 + 2\,\hat{\sigma}_1/\hat{\sigma}_2)^{-1} \tag{6.2}$$

6.2.2 *Rayleigh's formula*

In Maxwell's mixture formulation, the interaction between the particles is neglected. This is true only when θ is very small (on the order of 0.1). Under such low volume fraction of spherical conductor loading, Rayleigh [4] derived the following alternative relation:

$$(\hat{\sigma}_{eff} - \hat{\sigma}_1)/3\hat{\sigma}_1 \approx \theta\,(\hat{\sigma}_2 - \hat{\sigma}_1)/(\hat{\sigma}_2 + 2\hat{\sigma}_1) \tag{6.3}$$

6.2.3 *Fricke's formula*

Fricke extended the Clausius-Mossotti theory [5,6] for the dielectric constant and Lorentz-Lorenz theory [7,8] for the index of refraction to determine the effective conductivity of a dilute suspension of conducting particles in a homogeneous medium as given above. He also elucidated on similar considerations, the effective electric conductivity of a mixture constituted by shaped conducting inclusions (of spheroidal shape) suspended in a homogeneous medium. The relevant formulations are:

$$[(\sigma_{eff} - \sigma_1)/(\sigma_2 - \sigma_1)]\,[(\sigma_2/\sigma_1) - 1] = \beta\theta/(1 - \theta) \tag{6.4}$$

where

$$\beta = \frac{1}{3}\left[\frac{2}{1 + [(\sigma_2/\sigma_1) - 1]\,(M/2)} + \frac{1}{1 + [(\sigma_2/\sigma_1) - 1]\,(1 - M)}\right]\left(\frac{\sigma_2}{\sigma_1} - 1\right)$$

$M = [\phi - (\sin^3\phi)/2]/\sin^3\phi$ with $\cos\phi = a/b$, and $a < b$ (oblate spheroid); or
$M = [(1/\sin^2\phi') - \cos^2\phi'/2\sin^3\phi']\log_e[(1 + \sin\phi')/(1 - \sin^2\phi')]$ with $\cos\phi' = b/a$, and $a > b$ (prolate spheroid).

Here, a/b or b/a refers to the *aspect ratio* of the spheroidal particle.

Defining a shape parameter, x, as:

$$x = -\left\{\left(\frac{\sigma_2}{\sigma_1} - 1\right) - \left(\frac{\sigma_2}{\sigma_1}\right)\beta\right\} \Big/ \left\{\left(\frac{\sigma_2}{\sigma_1} - 1\right) - \beta\right\} \tag{6.5}$$

Equation 6.4 can be written as:

$$[(\sigma_{eff}/\sigma_1) - 1)]/[(\sigma_{eff}/\sigma_1) + x] = \theta\,[(\sigma_2/\sigma_1) - 1]/[(\sigma_2/\sigma_1) + x]$$

For a spherical case, $x = 2$; and, applied to the case of spherical (conducting) particulate suspensions in a dielectric host medium, the effective conductivity of the mixture reduces to:

$$[(\sigma_{eff}/\sigma_1) - 1)/[(\sigma_{eff}/\sigma_1) + 2] = \theta\,[(\sigma_2/\sigma_1) - 1]/[(\sigma_2/\sigma_1) + 2] \tag{6.6}$$

This is the well-known form of *Fricke's formula* [9,10], for a dielectric with spherical conducting inclusions.

6.2.4 *Bruggeman's formula*

Bruggeman assumed that for a given volume loading of spherical particles, the effective conductivity has a unique value $\hat{\sigma}_{eff}$; and every unit volume of this particulate loaded medium of a small volume δvol, with additional spherical particles of conductivity $\hat{\sigma}_2$ would augment the effective conductivity to $(\hat{\sigma}_{eff} + \delta\hat{\sigma}_{eff})$. Using this concept of proportional increments of effective conductivity *versus* volume loading of the inclusions, Bruggeman modified Rayleigh's formula and arrived at the following expression:

$$\sigma_{eff} = (\hat{\sigma}_{eff}/\sigma_1)^{1/3} [(\hat{\sigma}_1 - \hat{\sigma}_2)/(\hat{\sigma}_{eff} - \hat{\sigma}_2)] (1 - \theta) = 1 \tag{6.7}$$

With $|\hat{\sigma}_2| << (|\hat{\sigma}_1|$ *and* $|\hat{\sigma}_{eff}|)$, Equation 6.7 reduces to:

$$\hat{\sigma}_{eff} \approx \hat{\sigma}_1 (1 - \theta)^{3/2} \tag{6.8}$$

This equation corresponds to the case where the particles or grains act as insulators. Further, it suggests that if $\theta = 1$, $\sigma_{eff} \rightarrow 0$ and if $\theta = 0$, $\hat{\sigma}_{eff} \rightarrow \hat{\sigma}_1$, that of the host medium.

6.2.5 *Archie's law*

Equation 6.8 written in more generalized form as $\hat{\sigma}_{eff} \approx \hat{\sigma}_1 (1 - \theta)^{m_A}$ is found to be a good empirical fit for brine-saturated sedimentary rocks (with m_A in the range 1 to 5). This is known as *Archie's law* [12].

6.2.6 *Looyenga's formula/Böttcher's formula*

Using the concept of two concentric spheres of different conductivities, one enclosed within the other to represent a two-phase mixture, Looyenga [13] deduced the following mixture formula:

$$\theta = [(\hat{\sigma}_{eff} - \hat{\sigma}_1)(2\hat{\sigma}_{eff} + \hat{\sigma}_2)]/[3\, \hat{\sigma}_{eff}(\hat{\sigma}_2 - \hat{\sigma}_1)] \tag{6.9}$$

Independently, Böttcher [14] arrived at the same formulation from the considerations of internal field(s) associated with spherical particles.

6.2.7 *Lal and Parshad formula [15]*

Lal and Parshad [15] extended the dielectric-dielectric mixture theory to a dielectric-conductor composite, and derived an expression for the static (relative) permittivity of the mixture (ε_s) in terms of the volume ratio θ of the conductor inclusions:

$$\varepsilon_s = \varepsilon_{2s}/(1 - \theta)^B \tag{6.10}$$

In this relation, ε_{2s} is the static permittivity of the host dielectric and B is a shape parameter of the conducting particles related to the depolarization factors A_i *via* the relation given by:

$$B = (1/3) \sum_i A_i \tag{6.11}$$

Assuming the included particles as ellipsoids, the subscript i refers to the i^{th} axis of an ellipsoid with semiaxial lengths a, b, and c (see Figure 4.1). For a spheroidal particle $b = c$ and defining $x = a/b$, $x = 1$ specifies spherical particles. Prolate spheroidal particles with $x > 1$ will become needle-like fibers when $x >> 1$. Likewise, oblate spheroids with $x < 1$ will represent flaky, disk-like lamellae when $x << 1$. A_i can be evaluated by an integral relation due to Wallin [16].

It may be noted that Equation 6.10 cannot be extended to frequency-dependent, dynamic conditions; or is evaluation of B straightforward. Results presented in [15] are therefore based on an empirical value of B obtained *via* curve fitting to a set of test data.

6.2.8 *Scarisbrick and Kusy model*

Concerning the effective conductivity of a dielectric-conductor mixture, Scarisbrick [17] developed a random-chain model, to which Kusy [18] added a shape-dependent order function (U) established *via* probabilistic considerations. Again, the relevant expression refers only to d.c. conductivity of the mixture and is given by :

$$\sigma_{dc} = K^2 \sigma \theta (\theta)^{U\theta^{-2/3}} \tag{6.12}$$

where K is a constant decided by the conductive path cross-section. Further, σ and θ are the conductivity and volume fraction of the conducting inclusions.

6.2.9 *Frame and Tedford model*

Frame and Tedford [19] used Equations 6.10 and 6.12 to evaluate the static permittivity and d.c. conductivity of a composite made of alkyd resin loaded with graphite lamellae. In the relevant studies, the exponent B of Equation 6.10 was obtained by best-fitting the experimental data on static permittivity to the algorithm of Equation 6.10.

6.3 Complex Susceptibility Model: Neelakanta's Formula

Let ε and σ denote the relative (effective) permittivity and conductivity of the mixture. Subscripts 1 and 2 are used to specify the corresponding variables of the conducting inclusions and the dielectric matrix, respectively. The volume fraction of the inclusions is denoted by θ and U is an order function decided by the geometrical aspect ratio $(x = a/b)$ of the inclusions.

The electrical characteristics of a mixture formed by a random volumetric dispersion of shaped inclusions in a continuous host medium can be specified by the following functional relations:

$$F(\varepsilon) = \theta F(\varepsilon_1) + (1 - \theta) F(\varepsilon_2) \tag{6.13a}$$

and

$$G(\sigma) = \theta G(\sigma_1) + (1 - \theta) G(\sigma_2) \tag{6.13b}$$

Here, the functions F and G determine the law of mixing; and if they are known explicitly, the values of ε and σ can be determined uniquely. The law of mixing pertaining to a statistical mixture is constrained by: (1) Wiener's proportionality postulate* [20]; (2) Wiener's upper and lower bounds** on ε and σ; (3) the limiting values of $0 \le \theta \le 1$ and $0 \le U \le 1$; and (4) geometrical dissimilarity of the components in the mixture matrix.

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* *Wiener's proportionality postulation*: If the values of ε or σ of the constituents change in one and the same ratio, the values of ε or σ of the mixture should change identically.

** Wiener's upper and lower bounds: In an m-component mixture:

$$[1/\sum_{i=1}^{m}\theta_i p_i] \le p_{mixture} \le \sum_{i=1}^{m}\theta_i p_i$$

$$(p \Rightarrow \varepsilon \text{ or } \sigma)$$

The analytical endeavor of evaluating the functions F and/or G for various types of pure dielectric-dielectric mixtures resulted in several formulations; a comprehensive review of them has been published by Brown [21] and van Beek [22]. The contents of these reviews have also been reported by Tinga and Voss [23]. Relevant details are summarized in Chapter 5.

These formulations, however, ignore the statistical aspects of the mixture except the so-called logarithmic law of mixing due to Lichtenecker [24] and Lichtenecker and Rother [25]. This logarithmic law, however, does not take the particulate geometry into account and it lacks a linear form [26]. These deficiencies have, however, been offset by the author and others as reported in [27] and explained in Chapter 5.

The following analysis presented here refers to the author's contribution reported in [28], in which the logarithmic law is extended to a generalized electric susceptibility parameter χ pertaining to a dielectric plus conductor mixture subjected to complex field considerations. Hence, a dynamic model is presented to calculate the effective complex permittivity of dielectric-conductor mixtures.

The complex susceptibility of a conductor-loaded mixture can be specified as a logarithmic model in the following form:

$$\log \chi = \theta \log \chi_1 + (1 - \theta) \log \chi_2 \tag{6.14}$$

In terms of explicit parameters of the mixture constituents, namely, $(\varepsilon_1, \sigma_1)$ and $(\varepsilon_2, \sigma_2)$, Equation 6.14 can be written as

$$\chi = (\sigma_1/\omega\varepsilon_o)^\theta \exp(i\pi\theta/2) \{[(\varepsilon_2 - 1)^2 + (\varepsilon_2 \tan\delta_2)^2]^{1/2} \exp(-i\varphi)\}^{(1-\theta)} \tag{6.15}$$

where ε_o is the free-space permittivity, $\omega = 2\pi \times$ frequency, $\tan\delta_2$ $(= \sigma_2/\omega\varepsilon_o\varepsilon_2)$ is the loss tangent of the host medium and $\varphi = \tan^{-1}[\varepsilon_2 \tan \delta_2/(\varepsilon_2 - 1)]$.

Using the relation $(\varepsilon - 1) \equiv$ real part of χ, it follows that:

$$\varepsilon = (\sigma_1/\omega\varepsilon_o)^\theta [(\varepsilon_2 - 1)^2 + (\varepsilon_2 \tan\delta_2)^2]^{(1-\theta)/2} \cos[\pi\theta/2 + \varphi(1-\theta)] + 1 \tag{6.16}$$

The conductivity (σ) of the mixture can be extracted from the imaginary part of χ. Thus,

$$\sigma/\omega\varepsilon_o = (\sigma_1/\omega\varepsilon_o)^\theta [(\varepsilon_2 - 1)^2 + (\varepsilon_2 \tan\delta_2)^2]^{(1-\theta)/2} \sin[\pi\theta/2 + \varphi(1-\theta)] + 1 \tag{6.17}$$

Equations 6.16 and 6.17 should, however, be "weighted" to meet the limiting conditions, namely, $(\varepsilon, \sigma) = (\varepsilon_2, \sigma_2)$ at $\theta = 0$ and $(\varepsilon_1, \sigma_1)$ at $\theta = 1$.

Further, by including the geometrical dependence *via* an order function U in the logarithmic formulation of Equation 6.14, the following modified expressions for ε and σ are obtained on the basis of the arguments given by the author in [28].

$$\varepsilon_{mod} = C_1 [(\varepsilon - 1)^{U_\varepsilon} + 1] \tag{6.18}$$

and

$$\sigma_{mod}/\omega\varepsilon_o = C_2 [(\sigma_1/\omega\varepsilon_o)^\theta (\varepsilon_2 - 1)^{1-\theta} \sin(\pi\theta/2)]^{U_\sigma} + (\sigma_2/\omega\varepsilon_o) \tag{6.19}$$

under the valid assumptions that $\sigma_2 << \sigma_1$ and $\varepsilon_2 tan\delta_2 << (\varepsilon_2 - 1)$. Here, the coefficients C_1 and C_2 are parameters decided by the limiting conditions, namely, $\varepsilon = \varepsilon_2$ at $\theta = 0$ and $\sigma = \sigma_1$ at $\theta = 1$. Hence, they are specified explicitly as:

$$C_1 = \varepsilon_2 [(\varepsilon_2 - 1)^{U_\varepsilon} + 1]^{-1} \tag{6.20a}$$

and

$$C_2 = [(\sigma_1 - \sigma_2)/\omega\varepsilon_o] (\omega\varepsilon_o/\sigma_1)^{U_\sigma} \tag{6.20b}$$

The order functions U_ε and U_σ implicitly determine the dependence of ε and σ, respectively, on the geometrical aspect ratio x $(=a/b)$ of the particulate inclusion. Defining the particle eccentricity e $(=1 - b/a)$ when $b < a$ or $(a/b - 1)$ when $a < b$, the value of $e = 0$ corresponds to spherical particles; U_ε and U_σ should therefore be expressed in terms of e. That is, for a given eccentricity, the U_ε^{th} fraction of the stochastic system can be regarded as being polarized along the electric field and the $(1 - U_\varepsilon)^{th}$ fraction along the orthogonal direction. Likewise, U_σ should represent the fraction corresponding to current percolations.

On the basis of similarity to Maxwell-Boltzmann statistics applied to dipole orientation, the upper and lower bounds of the order function can be specified as follows:

$$U_U = [1 - L(e)/e]/2 \quad \cong (1/3) \quad \text{when } e \to 0 \tag{6.21a}$$

$$U_L = [(L(e)/e]/2 \quad \cong (1/6) \quad \text{when } e \to 0 \tag{6.21b}$$

where $L(e)$ is the Langevin function equal to $[coth(e) - 1/e]$. The functions U_ε and U_σ can be equated to U_L or U_U depending on the following states of the test mixture: For large values of $(\sigma_1/\omega\varepsilon_o\varepsilon_2)$, the composite can be considered as conductivity dominant; and for low values of $(\sigma_1/\omega\varepsilon_o\varepsilon_2)$, the mixture becomes permittivity dominant. Accordingly, the permittivity of the mixture as a function of frequency can be sketched as shown in Figure [6.1], indicating three zones, namely, the low-frequency, the high-frequency, and the intermediate (quasistatic) regions. It is, however, to be noted that the region-to-region transition is not abrupt. For calculation purposes, two corner frequencies, namely, ω_L and ω_H, can be approximately assigned marking the transitions as shown in Figure (6.1) since the regions are distinguishable in terms of $d\varepsilon'/d\omega$ slope. In summary, the complex permittivity spectra of a conductor-loaded mixture can be specified by the following:

(1) Complex permittivity of the mixture (ε):

$$\varepsilon = (\varepsilon' - i\varepsilon'') \tag{6.22a}$$

$$\varepsilon' = \{\varepsilon_2/[1 + (\varepsilon_2 - 1)^{U_\varepsilon}]\} \{[(\sigma_1/\omega\varepsilon_o)^\theta (\varepsilon_2 - 1)^{1-\theta} cos(\pi\theta/2)]^{U_\varepsilon} + 1\} \tag{6.22b}$$

$$\varepsilon'' = \sigma/\omega\varepsilon_o \tag{6.22c}$$

$$\sigma = (\sigma_1 - \sigma_2)\{[\omega\varepsilon_o(\varepsilon_2 - 1)/\sigma_1]^{1-\theta} sin(\pi\theta/2)\}^{U_\sigma} + \sigma_2 \tag{6.22d}$$

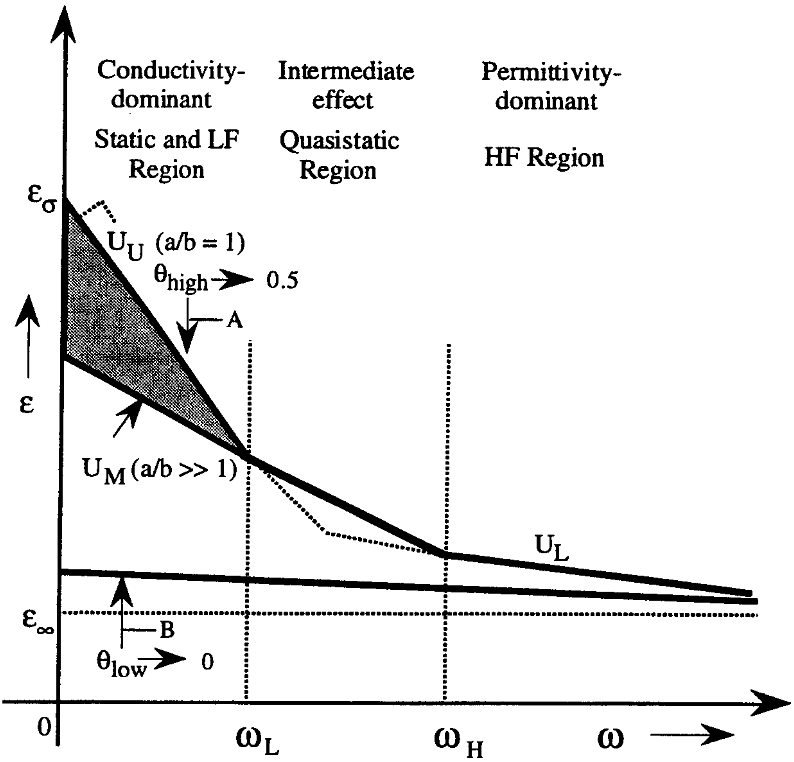

Figure 6.1 Permittivity *versus* frequency of a conductor-loaded dielectric.
A: For large volume fraction θ of inclusions.
B: For low volume fraction θ of inclusions.
The shaded region refers to the bounded range of values that ε may assume as described by the aspect ratio of the conducting inclusions ($1 \le a/b \ge \infty$).

(2) Order functions U_ε and U_σ at low frequencies $(\omega < \omega_L)$

$$U_\varepsilon = U_\sigma = \begin{cases} U_U = (1/2)[1 - L(e)/e] & e \cong 0 \\ U_M = (1/M) + (2-3M)/3 & e >> 1 \end{cases} \tag{6.23}$$

where $M = [(2 \pm e)/(3 \pm e) - L'(e)]^{-1}$ and $L'(e) = dL/de$; the positive sign here refers to $a/b < 1$ and the negative sign is for $a/b > 1$.

(3) Order functions U_ε and U_σ at high frequncies $(\omega > \omega_H)$:

$$U_\varepsilon = U_\sigma = U_L = (1/2)\,[(L(e)/e] \quad \text{for all values of } e \tag{6.24}$$

(4) Calculation of approximate values of ω_L and ω_H (Figure 6.1)

$$\omega_H \text{ is the solution of:} \qquad \varepsilon_{mod}(\text{with } U_L) \cong \varepsilon_{mod}(\text{with } U_U) \tag{6.25a}$$

and

ω_L is the solution of: $\varepsilon_{mod}(with\ U_L) \cong \varepsilon_{mod}(with\ U_M)$ (6.25b)

(5) Complex permittivity in the quasi-static range $(\omega_L < \omega < \omega_H)$:

$$\varepsilon' = \varepsilon_L' - (\varepsilon_L' - \varepsilon_H')\ [ln(\omega/\omega_L)]/[ln(\omega_H/\omega_L)] \quad (6.26a)$$

$$\varepsilon'' = \sigma/\omega\varepsilon_o\varepsilon' \quad (6.26b)$$

$$\sigma = \sigma_L - (\sigma_L - \sigma_H)\ [ln(\omega/\omega_L)]/[ln(\omega_H/\omega_L)] \quad (6.26c)$$

where $(\varepsilon_L', \sigma_L)$ and $(\varepsilon_H', \sigma_H)$ refer to values of (ε', σ) at ω_L and ω_H, respectively.

6.4 Direct-Current Conductivity

Equation 6.19 can be rewritten to represent the static conductivity (σ_{dc}) of the mixture. The d.c. condition refers to the limiting case of $\omega \rightarrow 0$, or a factor τ_o (which is extremely large) should replace $\omega/2\pi$ in Equation 6.19. The factor to can be evaluated under the condition $x \rightarrow 1$, $\theta \rightarrow 1/2$, $U_\sigma \rightarrow 1$ and $\sigma_{dc} \cong (\sigma_1\sigma_2)^{1/2}$, representing the weighted-average value. It is found that

$$\sigma_{dc} \cong (\sigma_1 - \sigma_2)\ \{[2\pi\varepsilon_o(\varepsilon_2 - 1)/\sigma_1\tau_o]^{1-\theta} \sin(\pi\theta/2)\}^{U\sigma} + \sigma_2 \quad (6.27a)$$

with

$$\tau_o = \frac{\pi\varepsilon_o(\varepsilon_2 - 1)}{\sigma_2} \frac{\sigma_1^{1/2} + \sigma_2^{1/2}}{\sigma_1^{1/2} - \sigma_2^{1/2}} \quad (6.27b)$$

and

$$U_\sigma = U_U = 1/2[1 - L(e)/e] \quad (6.27c)$$

6.5 Results Pertinent to Complex Susceptibility Model

The formulations presented in Section 6.3 and 6.4 have been verified by comparing the computed results obtained for a set of dielectric-conductor mixtures with the corresponding measured data available in the literature. Relevant results are presented in Table 6.1 and 6.2. Pertinent conclusions have been comprehensively discussed in [28].

6.6 Percolation Model(s)

The critical behavior of the dielectric permittivity of metal-insulator composites near the percolation threshold of conduction has been studied by Grannan et al. [30] using samples of a KCl matrix dispersed with small silver particles. Relevant studies indicate empirically that the dielectric constant obeys a scaling relation with a critical exponent factor, s. The following is the expression for the effective dielectric comstant of the metal-insulator mixture:

$$\varepsilon_{eff} = C[(\theta_c - \theta)/\theta_c]^{-s} \quad (6.28)$$

where C is a constant prefactor, θ is the volume fraction of the metal in the composite, θ_c is the critical volume fraction at which conduction begins and s is a critical exponent. The above scaling relation (Equation 6.28) is characterized by the critical exponent which resembles that observed in thermodynamic phase transitions.

Doyle and Jacobs [31] developed an effective cluster model to described the dielectric enhancement in metal-insulator composities. The basis for their model is as follows: Disordered suspensions contain a wide range of particle clusters of various sizes and shapes, composed of varying numbers of spheres in different spatial arrangements. Relevant to this type of metal-insulator mixtures, the effective permittivity (ε_{eff}) was deduced by modifying the Clausius-Mossotti equation with the inversion of a polarization parameter, β. The relevant expression is given by:

$$\varepsilon_{eff} = \varepsilon_n[1 + 3\beta/(1 - \beta)] \tag{6.29}$$

where ε_n is the permittivity of the host medium and β is explicitly given by:

$$\beta = \theta\{1 + (\theta/\theta_c)\,[(1/\theta_c) - 1]\} \tag{6.30}$$

Again, the value of θ_c is empirically deduced from experimental data. The above mode is shown to fit a disordered suspension or mesosuspension of isolated conducting spheres and localized spherical, closely packed metallized clusters with a wide range of radii suspended in a background host dielectric.

While the above models refer to effective permittivity of metal-insulator mixtures, electrical resistivity (or conductivity) of such mixtures has been modeled by McLachlan et al. [32,33] *via* a general effective media approach combining percolation theory principles and effective media theories. The resulting formulations are elaborated in [32,33].

Chen and Johnson [34] have developed a model to describe the a.c. electrical properties of random metal-insulator composites wherein the metallic inclusions are filamentary or modular shapes. Again their model is based on power-law considerations pertinent to percolation principles.

6.7 Sillars' Model

Sillars [35] developed a model to describe the properties of a dielectric containing semiconducting particles of various shapes. His study reports Wagner's model and indicates the significant influence of conducting shaped particles (such as spheroidal particles) on the effective conductivity of dielectric-conductor mixtures.

6.8 Multilayered Conducting Dielectrics

A pertinent model to describe the effective permittivity characteristics of multilayered conducting dielectrics has been developed by Ongara [36] by exactly solving for Debye-like relaxation in such composites.

6.9 Granular Films of Conductor-Insulator Mixtures

Cohen et al. [37] portrayed the electromagnetic characteristics of granular silver and gold films by deducing their electrical properties *via* generalized Maxwell-Garnett theory.

The microstructural effects on the dielectric properties of granular composite films has been considered by Sheng [38] who deduced the effective dielectric function of such materials using Maxwell-Garnett theory.

6.10 Conclusions

From the various models discussed, it can be observed that the studies concerning dielectric-conductor mixtures are not totally comprehensive. Most of the models are empirical and are approximate. Further, the frequency dependency characteristics of such mixtures are far more incomplete. Closed-form expressions available offer results over only a limited range of frequencies and/or volume fractions. Studies on the shape dependency of the effective parameters are also significantly limited. Considering the fact that conductor plus insulator composites have wide applications in electromagnetic technology, the research in this area (though a century old) is rather incomplete, and offers a niche for futuristic in-depth studies.

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Defining Terms

Aspect ratio: The ratio of the largest dimension to the smaller dimension of a two- and/or three dimensional body.

Dielectric-conductor mixture: A two-phase mixture system constituted by a dielectric receptacle hosting a dispersion or a textured arrangement of discrete conducting inclusions.

Form factor (shape factor): A numerical value denoting the shaped extent of a nonspherical particle.

Percolation: A phenomenon in which the flux percolates or proliferates across a medium along random paths.

Table 6.1 Measured and Computed Data: Permittivity of Dielectric-Conductor Mixture

Mixture				Calculated Data on ε				Measured Data on ε	
				Method of [28]		Other Method(s)			
Host Dielectric Medium (ε_2)	Conducting Inclusions (σ)	Frequency (Hz)	Volume Fraction of Inclusions, θ	ε	Remarks	Semiempirical Best-fit data (ε)	Remarks	ε	Remarks
Alkyd resin (3.86)	Graphite lamellae (200 S m^{-1}) Aspect ratio a/b<<1	10^3	0.007	4.02	a/b = 1/13	4.01	b/a = 13	4.01 ± 6%	
			0.200	4.34	$U_\varepsilon = U_M$	4.37	Shape factor	4.37 ± 6%	[19]
			0.060	5.63		5.66	B = 6.2	5.66 ± 6%	
			0.130	9.39		9.15	[3]	9.15 ± 6%	
			0.170	12.87		12.25		12.25 ± 6%	
			0.250	25.09		22.97		22.97 ± 6%	
Epoxy (3.81)	Aluminum needles (3.77×10^7 S m^{-1}) a/b>1	1.6×10^6	0.050	4.56	B = 4.42	4.59	Logarithmic model [16]	4.71	
			0.100	5.57	a/b = 1.5	5.55	$\varepsilon_1 = 165$	5.60	[29]
			0.150	6.94	$U_\varepsilon = (U_L U_U)^{1/2}$	6.70	Empirical value	7.10	
			0.200	8.78		8.09	unjustifiably presumed in [16]	8.18	
			0.250	11.25		9.77	$\varepsilon_2 = 3.81$	9.16	
			0.300	14.50		11.80		12.05	

(continued..)

Table 6.1 Measured and Computed Data: Permittivity of Dielectric-Conductor Mixture

Mixture				Calculated Data on ε				Measured Data on ε	
				Method of [28]		Other Method(s)			
Host Dielectric Medium (ε_2)	Conducting Inclusions (σ)	Frequency (Hz)	Volume Fraction of Inclusions, θ	ε	Remarks	Semiempirical Best-fit data (ε)	Remarks	ε	Remarks
Aetna oil (2.21)	Mercury drops (10^6 S m^{-1}) a/b ≅ 1	10^3	0.015	2.29	a/b = 1	2.31	a/b = 1	2.31	Data due to Guillein as reported in [15]
			0.049	2.50	$U_\varepsilon = U_L$	2.57	Shape factor	2.57	
			0.171	3.80		3.88	B = 3	3.94	
			0.250	5.04		5.24	[14]	5.34	
			0.329	6.98		7.30	(Bruggeman's	7.15	
			0.401	9.45		10.27	formula)	9.67	
Mineral oil (2.1)	Iron spheroidal particles (10^7 S m^{-1}) a/b > 1	10^3	0.050	2.46	a/b = 1.3		a/b > 1	2.60	Data due to Nasuhoglu as reported in [15]
			0.100	2.93	$U_\varepsilon = U_L$		Shape factor	3.30	
			0.150	3.57			B ≅ 3.96	4.00	
			0.200	4.47			[14]	4.90	
			0.250	5.56			(Bruggeman's formula)	6.25	

Table 6.2 Measured and Computed Data: Dynamic Response of Dielectric-Conductor Mixture

Mixture			Calculated and Measured Data on Mixture Permittivity (ε)												
			$\theta = 0.007$[a]		$\theta = 0.020$		$\theta = 0.060$		$\theta = 0.130$		$\theta = 0.170$		$\theta = 0.250$		
Host Dielectric Medium (ε_2)	Conducting Inclusions (σ)	Frequency (Hz)	I[b]	II[c]	I	II	I	II	I	II	I	II	I	II	U_ε
Alkyd resin (3.86)	Graphite lamellae (200 S m^{-1})	10^1	4.60	4.03	4.80	4.40	6.60	5.87	10.00	10.46	13.20	14.98	28.60	31.86	U_M
	Aspect ratio a/b << 1	10^2	4.50	4.02	4.70	4.35	6.40	5.63	9.70	9.44	13.00	13.00	27.70	25.55	
	In the calculations a/b = 1/13	10^3	4.40	4.02	4.60	4.34	6.20	5.63	9.40	9.39	12.80	12.87	26.80	25.09	U_L
	In data of [19]	10^4	4.30	4.00	4.50	4.30	6.00	5.60	9.10	9.30	12.50	12.80	25.40	25.00	
	a/b = 1/13	10^5	4.10	4.00	4.40	4.30	5.90	5.60	8.70	9.30	12.00	12.80	25.00	25.00	

a Volume fraction of the inclusion: θ.
b Experimental results due to Frame and Tedford [19]: I.
c Calculated data as per the author's method [28]: II.