Designing Dielectric Loss at Microwave Frequencies using Multi-Layered Filler Particles in a Composite

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ABSTRACT

Microwave-absorbing materials find application in telecommunications, microwave heating and for representing the behavior of biological tissue in the presence of microwave radiation. Commonly, such materials are formed using ferromagnetic filler particles and rely on the phenomenon of ferromagnetic resonance for absorption of microwaves. Dielectric loss at microwave frequencies can be engineered through creating a phase lag, with respect to the applied electric field, of the movement of free charges in a composite formed using metal-coated filler particles. These materials can be engineered to be less dense and, therefore, more lightweight than those formed with ferromagnetic fillers, which is an advantage in some applications. Furthermore, theory shows that the frequency of maximum absorption can be tailored by selecting the conductivity and thickness of the particle coating although, in practice, it may be difficult to fabricate particles with tightly controlled physical parameters. In this work, theories for calculating complex permittivity of composites with layered filler particles are reviewed, and experimental observations of dielectric relaxation in composites formed by dispersing tungsten-coated glass bubbles in paraffin wax are shown.

Index Terms — **Composite material, Dielectric relaxation, Microwaves, Dielectric loss, Multi-layered filler particles**

1 INTRODUCTION

MATERIALS which exhibit dielectric relaxation at microwave frequencies are potentially useful as absorbers for reducing cross-talk and interference in telecommunications [1, 2], for improving heat transfer in the packaging of microwave foods [3], and as phantoms mimicking the behavior of human tissue exposed to microwave radiation, e.g. [4, 5]. Absorption of microwave radiation is commonly achieved using composite materials consisting of ferromagnetic filler particles (e.g. iron, cobalt or nickel) dispersed in a suitable matrix [6, 7]. The absorption mechanism in this case relies on the phenomenon of ferromagnetic resonance in the filler particles [8]. These composites have proved reliable but are typically dense and consequently heavy. Many applications would benefit from lightweight materials for absorption of microwave radiation, achievable by relying on dielectric, rather than magnetic, loss as the primary absorption mechanism.

Dielectric relaxation, observed in measurements of relative permittivity of a composite material consisting of homogeneous, conductive filler particles dispersed in an essentially non-conductive matrix, is associated with entrapment of free charges at the interfaces between the constituent phases. The resulting interfacial polarization increases the low-frequency permittivity of the composite, compared with the permittivity of the unfilled matrix material. At low frequencies, the movement of free charge follows the cycle of the applied electric field with little or no phase lag. As the frequency is increased, a characteristic relaxation frequency, υ_{rel}, is reached at which the induced polarization is $\pi/4$ out of phase with the applied field. This is the frequency at which absorption loss is maximum. As the frequency increases still further, the phase lag between the applied electric field and the induced polarization continues to grow until, in the high-frequency regime, the conductive phase behaves as a lossless dielectric and interfacial polarization does not occur. For recent reviews of electrical properties and modelling of dielectric mixtures see references [9] and [10]. Dielectric relaxation due to interfacial polarization can be tuned to a specific frequency by selecting the conductivity of the filler particles. For example, calculations of the optical extinction coefficient for spherical copper particles dispersed in fluorozirconate glass [11] indicate that dielectric relaxation of the composite occurs at approximately 4.6×10^{14} Hz. Similar behavior is obtained with other metal fillers. Modelling predicts that, in order to achieve dielectric relaxation at microwave frequencies, due to an interfacial polarization process

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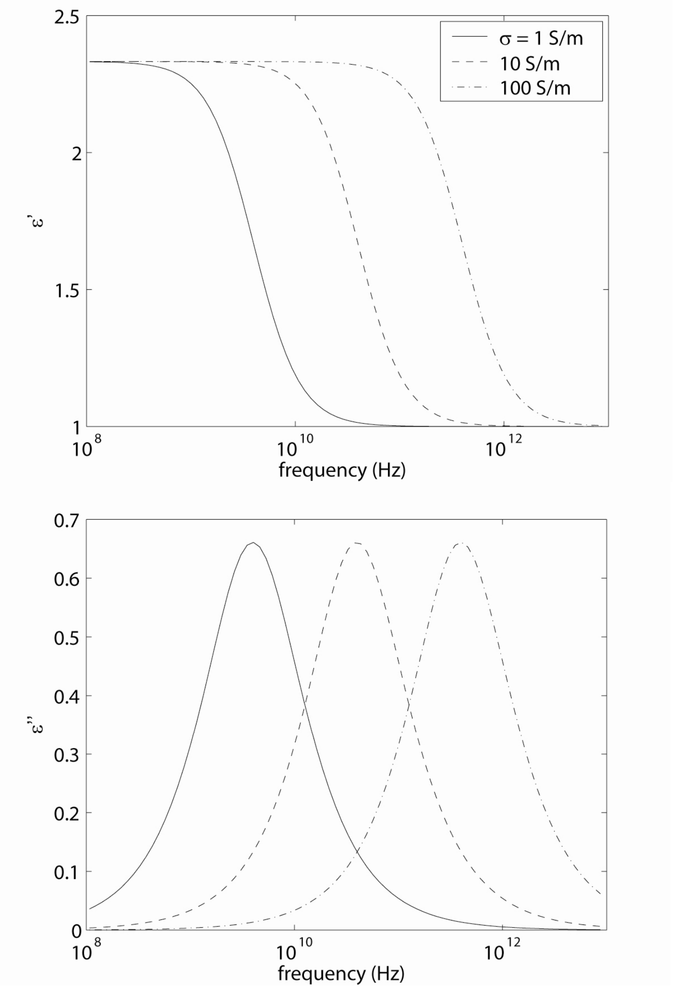

Figure 1. Real and imaginary parts of bulk permittivity for a composite material containing homogeneous, conductive, spherical filler particles. σ_{filler} = 1, 10 and 100 S/m. $\varepsilon'_{\text{filler}} = \varepsilon'_{\text{matrix}} = 1$. The filler volume fraction, *f*, is 0.3.

in a composite containing homogeneous filler particles, the particles should have conductivity in the approximate range 1 to 100 S/m. This is illustrated in Figure 1, in which the bulk relative permittivity of a composite is calculated for spherical filler particles with conductivities 1, 10 and 100 S/m. From the Maxwell-Ampère law applied to a time-harmonic excitation, with time-dependence $e^{-i\omega t}$, and the constitutive relation connecting the electric flux density and the electric field, a complex relative permittivity may be defined

$$\varepsilon = \varepsilon' + i\varepsilon'' \text{ with } \varepsilon'' = \frac{\sigma}{\omega\varepsilon_0} \tag{1}$$

In equation (1), σ is the conductivity of the medium, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free space and $\omega = 2\pi\upsilon$ is the angular frequency. This means that, in the frequency range 10^8 to 10^{13} Hz shown in Figure 1, the conductive filler behaves as a good conductor at the low end of this frequency range and as a poor conductor, or insulator, at the high end of this frequency range. This behavior may be explained in terms of the loss angle of the filler material, defined

$$\theta_{filler} = \arctan\left(\frac{\varepsilon''_{filler}}{\varepsilon'_{filler}}\right) = \arctan\left(\frac{\sigma_{filler}}{\omega\varepsilon'_{filler}\varepsilon_0}\right), \tag{2}$$

which varies from approximately π/2, for $\sigma_{filler}/(\omega\varepsilon_0) >> \varepsilon'_{filler}$ at the low end of this frequency range, to approximately zero, for $\sigma_{filler}/(\omega\varepsilon_0) << \varepsilon'_{filler}$ at high frequency. The curves shown in Figure 1 are calculated with a model in which the particles are represented by multipole sources located at their centers [12], although for this system, in which the volume fraction $f = 0.3$, $\varepsilon'_{\text{filler}} = 1$ and $\varepsilon'_{\text{matrix}} = 1$, essentially identical results are obtained with effective medium formulas, e.g. [13]. Figure 1 shows that as the conductivity of the particles is increased by a factor of ten, say, so the frequency of relaxation increases by the same factor. In fact, the frequency at which relaxation occurs is proportional to the particle conductivity; $\upsilon_{\text{rel}} \propto \sigma$ [14].

Materials with conductivity in the range 1 to 100 S/m are not readily available as fillers for composite materials, although dielectric relaxation in the frequency range 8.2 to 12.4 GHz has been observed in composites with nano Si/C/N and nano SiC filler particles [15], and at around 1 GHz with ferroelectric polycrystalline ceramic fillers [16]. An alternative means of creating dielectric relaxation in the microwave frequency range is to employ non-conductive filler particles that are coated with a thin conductive layer. The relaxation frequency observed in these kinds of composites is now governed by the thickness, as well as the conductivity, of the conductive shell. Indeed, for very thin metal films the conductivity and film thickness are related [17, 18]. Dielectric relaxation in these kinds of composites has been observed experimentally in the microwave [19] and optical/infrared [20-22] regions of the frequency spectrum. Practically, the conductive coating on the substrate particles may be discontinuous. In this case, the frequency at which relaxation occurs also depends on the area fraction and percolation threshold of the coating [23, 24].

In this article, dielectric relaxation in a composite due to polarization at the interfaces of layered filler particles – essentially conductive shells – is explored both theoretically and with reference to experimental measurements. For brevity, this article focuses on isotropic materials in which the filler particles are multi-layered spheres. For work describing materials with other types of inhomogeneous filler particles, see for example references [13] (spherical inclusions with radially linear, parabolic and Gaussian permittivity profiles) and [25] (cylindrical inclusions with radially exponential, linear and power-law permittivity profiles). Composite materials exhibiting anisotropic dielectric behavior can be created by embedding partially- or fully-aligned non-spherical multi-layered particles in a matrix. See for example references [12] and [26-31].

2 MODELLING DIELECTRIC RELAXATION IN COMPOSITES WITH MULTI-LAYERED FILLER PARTICLES

2.1 REVIEW

A single or dual dielectric loss process can arise in a composite consisting of coated filler particles dispersed in a matrix, depending on the dielectric and geometric properties of the particle core and layer. This effect has been investigated theoretically by means of both dipole [32] and multipole [12, 26] representations of the electric potential in a composite system in which the filler particles are coated spheres and, in the case of multipoles, spheroids. At optical and infrared frequencies, the phenomenon has been modelled using the Maxwell-Garnett effective medium relation [11], Mie scattering theory [11, 20] and a time-dependent density functional method [33].

Tinga *et al* [27] give a closed form solution to the problem of multiphase inclusions in the form of confocal ellipsoidal shells dispersed in a host material. First-order inclusion interactions are implicitly contained in the solution by choice of the boundary conditions. A self-consistent solution for the dielectric constant of the mixture is then obtained without explicitly solving for the electric field values. The work is motivated by the desire to model the dielectric constant of wood (a mixture of cellulose, air and water) for the purpose of determining water content. In the theoretical approach, an extra boundary between the inclusions is specified which allows interaction effects to be accounted for. This boundary encloses a representative volume, which is the total volume divided by the number of inclusions, and it is assumed that a single particle lies centrally in the volume. The geometry of the volume - here an ellipsoid confocal with the inclusion – is chosen for mathematical convenience. Within the representative volume, but exterior to the particle, the permittivity takes the value of the matrix material. Outside the representative volume, the permittivity is assigned the effective value of the composite. According to Landauer's review article [34] this approach, like Lorentz's treatment of spherical particles embedded in a matrix, suffers from the assumption that the particles acting on the representative particle behave as point dipoles. If the particles occupy a region of space sufficiently small that this assumption is reasonable, then the very interaction which is being assessed becomes negligible. In addition, for shapes other than spheres, the point dipole approximation can be very poor due to possibly rapid local fluctuations in the electric potential in the neighborhood of the particles. These rapid fluctuations cannot be adequately described by a dipole approach. Another difficulty is that for any appreciable volume fraction of particles the shell boundary cuts right through some of them.

Sihvola and Lindell [13] obtain the polarizability and dipole moment of different types of small, inhomogeneous inclusions and, from the dipole moment, solve for the effective permittivity of a dielectric mixture that contains these inclusions. Results for multi-layered and inhomogeneous inclusions with linear, parabolic and Gaussian permittivity profiles are presented. The spatial correlation distance of the material is restricted to be much smaller than the wavelength of the applied field. This quasistatic restriction means that scattering losses are not included in the effective permittivity calculation, but absorption losses are taken into account.

The complex dielectric constant of a composite with an interlayer separating the matrix and particle phases was studied by Steeman and Maurer [35] as a function of the volume fractions and the properties of the filler, interlayer and matrix. An analytical expression describing the influence of an interlayer on the dielectric constant of the composite as a function of the volume fraction and interlayer properties is described. The theoretical approach is similar to that of Tinga *et al* [27]. The work is motivated by the practical concern of the adverse effect, on the properties of some composites, of adsorbed water at the interface between filler and matrix. The presence of water can be detected very sensitively using dielectric measurement techniques. The authors of reference [35] mention work of Pauly and Schwan [36] and Hanai [32] in which analytical expressions for the dielectric behavior of suspensions of spherical particles with a surface layer are given. In references [36] and [32] it is shown that, for constituents with frequency-independent material properties, in general two relaxation processes exist.

More recently, the models of Tinga *et al* [27] and Sihvola and Lindell [13] have been employed by Friedman [37] to improve understanding of the relation between the effective dielectric constant of soils and their water content.

A topic of increasing interest is the effect of the interface region between two, say, components of a composite system. Chemically, this region is likely to exhibit dielectric properties which differ from those of the bulk matrix material, perhaps due to alignment of polymer chains near the surface of a filler particle, or other chemical processes. Especially for composites with small (nanoscale) filler particles, the presence of these ‘interphase’ regions may have a significant, or even dominant, effect on the dielectric properties of the bulk material [38, 39]. Power-law relationships for modelling dielectric properties of two-phase composite systems have been extended by Todd and Shi to take into account interactions between the components in the form of interphase regions [40]. If overlap between the interphase regions surrounding each filler particle is not permitted, this formulation provides a mathematical description of the dielectric behavior of a composite with coated filler particles.

Calculations of the optical extinction coefficient for spherical, copper-coated dielectric particles in fluorozirconate glass are presented by Edgar [11]. Two methods of calculation are compared; one based on a modern discussion of the general theory of light scattering from a particle embedded in a homogeneous material [41] and the other based on the Maxwell-Garnett theory. The comparison indicates that effective medium theory is useful for composites whose filler particles are small compared to the interrogating wavelength, although it is of decreasing accuracy as the size of the particle increases relative to the wavelength. This is to be expected since light incident on a slab of glass containing particles whose dimensions are of the order of a wavelength, or greater, will be attenuated by the combined effects of scattering and absorption, whereas the Maxwell-Garnett theory accounts only for absorption. Edgar's study is motivated by evidence for copper occurring as a coating on dielectric crystallite impurities in fluorozirconate glass - a substance used to make optical fibers.

Optical absorption spectra for metal nanoshells have been calculated by Halas *et al* using two methods. A generalized Mie scattering approach, in which line-broadening mechanisms are included, is adopted in references [20, 42, 43]. Classical Mie scattering theory requires, as an input, the frequency-dependent dielectric function of the filler particles. To overcome the need for this function, which is often known for bulk materials but cannot be used with confidence for nanoscale particles, a time-dependent density functional method for calculation of the optical properties of metal nanoshells is adopted in reference [33].

2.2 MULTIPOLE AND DIPOLE THEORIES

Three theoretical descriptions of the bulk permittivity of a composite material, representing different levels of approximation, are summarized in the following paragraphs. First, the multipole theory of reference [12], accurate to order $(f)^{14/3}$, is given. Then it is shown how this result reduces to that obtained by Sihvola and Lindell [13] if the particle volume fraction is sufficiently low that the local field at a representative particle is perturbed only slightly by the presence of its neighbors. In this case the particles may be modelled as interacting dipole sources. If the filler particles are well-separated, it may be assumed that the perturbation of the local field at a representative particle, due to its neighbors, is negligible. Then the particles may be treated mathematically as non-interacting dipole sources and the result is simplified still further [44]. In all three approaches it is assumed that the particles are significantly smaller than the wavelength of the electromagnetic radiation and that scattering losses are negligible. The electric scalar potential is then Laplacian and the mathematical treatment is as for a static system. It is also assumed that the electromagnetic skin depth in the conductive phase (defined as $\delta = [2/(\omega\mu\sigma)]^{1/2}$ with μ being the magnetic permeability of the conductor) is significantly larger than the thickness of the conductive phase. Further, the intrinsic material parameters ε' and σ are assumed constant over the frequency range considered.

Consider a collection of identical, coated, spherical filler particles arranged on a simple-cubic lattice whose lattice vectors coincide with the axes of a Cartesian co-ordinate system, as shown in Figure 2. Symmetry dictates that, when an electric field is applied in the direction of any of the three co-ordinate axes, the same value of bulk permittivity, ε, is observed. An expression for ε may be obtained by treating the particles as multipole sources located at their centers, resulting in the following series solution [12].

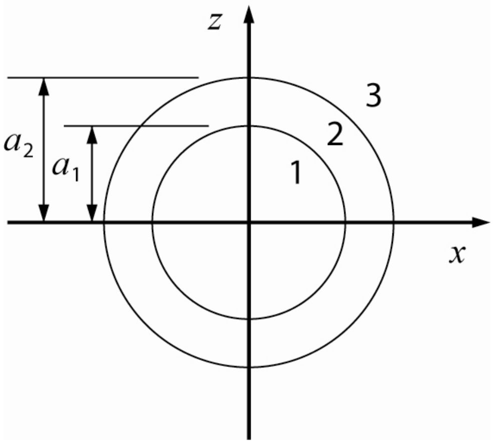

Figure 2. Cross-section of a coated sphere. Region 1 denotes the particle core, 2 the coating and 3 the interstitial matrix. a_1 is the core radius and a_2 the radius of the entire (coated) particle.

$$\frac{\varepsilon}{\varepsilon_3} = 1 - 3f\left[\frac{1}{L_1^{23}} + f + c_1 f^{10/3} + c_2 f^{14/3} + O\left(f^{18/3}\right)\right]^{-1} \tag{3}$$

In equation (3), f is the particle volume fraction, ε_3 is the relative permittivity of the matrix and L_1^{23} is a coefficient arising from the application of continuity conditions on the electric potential at the interface between the layer at the surface of the particle and the matrix, regions 2 and 3. This and the c_i are functions of the dielectric properties and volume fractions of the individual phases, and are detailed in the Appendix. If any of the individual phases are lossy, with complex ε_i, then ε will also be complex. Equation (3) is an extension of the result of reference [45] for homogeneous spherical filler particles, to spherical filler particles with a surface layer.

The series in equation (3) has been truncated to allow analytical calculation of the coefficients [12]. Coefficients of higher-order terms could be calculated numerically if desired. Despite being truncated, equation (3) is more accurate than alternative approaches discussed in section 2.1 for calculating the effective permittivity of a composite with spherical particles arranged on a simple-cubic lattice.

If the particle volume fraction is sufficiently low that the local field at a representative particle is perturbed only slightly by the presence of its neighbors, the particles may be modelled as interacting dipole sources. Then the first two terms in square brackets of equation (3) are obtained. Expanding L_1^{23} then gives the following expression for ε:

$$\frac{\varepsilon}{\varepsilon_3} = 1 + 3\left[f(\varepsilon_1+2\varepsilon_2)(\varepsilon_2-\varepsilon_3)+f_1(\varepsilon_1-\varepsilon_2)(2\varepsilon_2+\varepsilon_3)\right] / \begin{bmatrix} (\varepsilon_1+2\varepsilon_2)(\varepsilon_2+2\varepsilon_3)+2(f_1/f)(\varepsilon_1-\varepsilon_2)(\varepsilon_2-\varepsilon_3) \\ -f(\varepsilon_1+2\varepsilon_2)(\varepsilon_2-\varepsilon_3)-f_1(\varepsilon_1-\varepsilon_2)(2\varepsilon_2+\varepsilon_3) \end{bmatrix}. \tag{4}$$

The f_i are volume fractions of the individual phases, $i = 1,2,3$. The volume fraction of the coated particle is $f = f_1 + f_2$. The ε_i are relative permittivity values. The result shown in equation (4) is identical to that obtained by Sihvola and Lindell [13] for a mixture of coated spheres dispersed in a matrix in which the only restriction on microstructure is related to the assumption that the particles behave as interacting dipole sources.

If the filler particles are well-separated, it may be assumed that the perturbation of the local field at a representative particle, due to its neighbors, is negligible. Then the particles may be treated mathematically as non-interacting dipole sources and only the first term in square brackets of equation (3) is obtained. An equivalent result is obtained in reference [44] for homogeneous filler particles. This leads to the loss of the last two terms in the denominator of the term on the right-hand side of equation (4), which then reduces to

$$\frac{\varepsilon}{\varepsilon_3} = 1 + 3\left[f(\varepsilon_1+2\varepsilon_2)(\varepsilon_2-\varepsilon_3)+f_1(\varepsilon_1-\varepsilon_2)(2\varepsilon_2+\varepsilon_3)\right] / \left[(\varepsilon_1+2\varepsilon_2)(\varepsilon_2+2\varepsilon_3)+2(f_1/f)(\varepsilon_1-\varepsilon_2)(\varepsilon_2-\varepsilon_3)\right]. \tag{5}$$

Equation (5) is generally considered accurate for volume fraction no greater than 0.3 [44]. For larger volume fractions, the effect of composite microstructure is significant and needs to be taken into account as, for example, in the development of equation (3).

2.3 EXAMPLES

For composites whose filler particles have continuous conductive coatings, modelling reveals that the frequency at which interfacial-polarization relaxation occurs depends on both the conductivity of the coating and its thickness relative to the particle radius. Referring to Figure 2 the following ratio is defined:

$$t = \frac{a_2 - a_1}{a_2}. \tag{6}$$

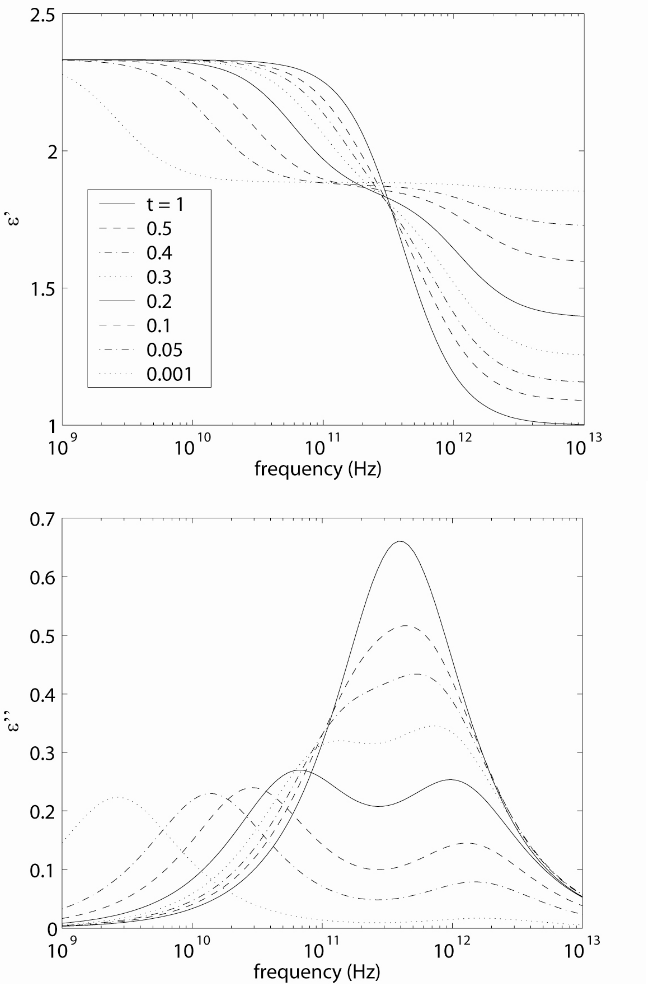

Figure 3. Real and imaginary parts of bulk permittivity for a composite material containing spherical filler particles, as a function of frequency and ratio of shell thickness to particle radius, t. $\varepsilon_{core} = 10$, $\varepsilon_{shell} = 1 + i100/(\omega\varepsilon_0)$ and $\varepsilon_{matrix} = 1$. $f = 0.3$.

In Figure 3, the bulk relative permittivity of a composite is shown for spherical filler particles with values of t ranging from 1 (homogeneous particle) to 0.001, for filler volume fraction $f = 0.3$. The permittivity value of the matrix material is assumed equal to that of free space, ε_0. The relative permittivity of the particle core is $\varepsilon_{core} = 10$, and the complex relative permittivity of the particle shell is $\varepsilon_{shell} = 1 + i100/(\omega\varepsilon_0)$, such that the particle shell has the same properties as the homogeneous filler particles with $\sigma = 100$ S/m, whose dielectric response is shown in Figure 1. The curves are calculated according to the multipole theory of equation (3). It can be seen that, as the layer thickness is reduced, the high-frequency limiting value of the real permittivity increases. This is due to the increasing volume fraction of the particle core, as t decreases. Two relaxation peaks can be distinguished in cases where the filler particles are inhomogeneous. This is a consequence of the fact that the real part of ε_{core} is greater than that of ε_{shell} [26]. This kind of fine structure may only be observed experimentally in the case of a well-controlled system of particles in which t is tightly specified. In practice, variations in coating thickness, uniformity and, to a lesser extent, particle size cause broadening of the relaxation [19, 42]. Nonetheless, the results of Figure 3 show that the frequency of dielectric relaxation observed in a composite material can be reduced by using conductive-shell filler particles rather than homogeneous conductive particles. This deduction is in agreement with that made in modelling optical responses of composites with metal-shell filler particles, even when scattering losses are taken into account [11, 20-22].

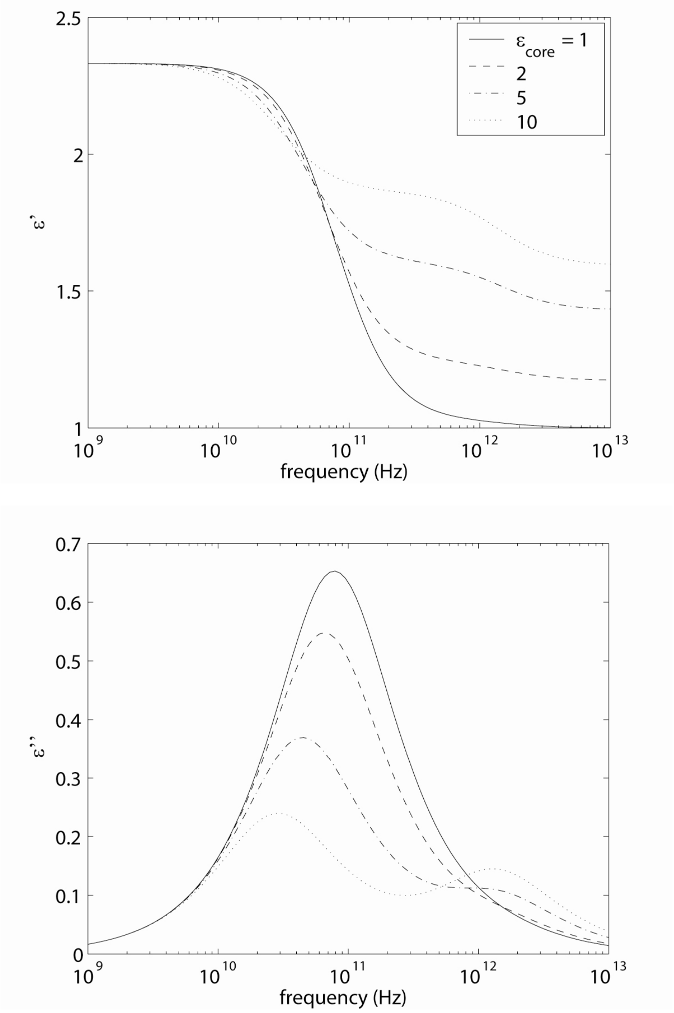

Figure 4. Real and imaginary parts of bulk permittivity for a composite material containing spherical filler particles, as a function of frequency and dielectric constant of the particle core, ε_{core}. $\varepsilon_{shell} = 1 + i100/(\omega\varepsilon_0)$ and $\varepsilon_{matrix} = 1$. $f = 0.3$.

Changing the conductivity of the coating gives rise to similar behavior as for the composite with solid filler particles, shown in Figure 1. That is, $\upsilon_{rel} \propto \sigma_{shell}$. Very thin metal coatings exhibit conductivity which is significantly reduced compared with the value for the bulk metal [17, 18], giving rise to the possibility that metal-coated particles embedded in a host medium will produce dielectric relaxation at microwave frequencies.

In Figures 4 and 5, the effect of changing the dielectric constant of the particle core and the matrix, respectively, on the bulk permittivity of the composite is shown. The particle coating has the same dielectric constant as that in Figure 3, and $t = 0.1$. From Figure 4 it is seen that increasing the value of ε_{core} has the effect of increasing the high-frequency asymptotic value of ε', whereas the low-frequency value is not affected by changes in ε_{core} for the system considered here. This is due to shielding of the core by the conductive layer in the low-frequency regime, where the loss angle $\theta_{shell} \approx \pi/2$. In the high-frequency regime, the shell behaves as a dielectric and no longer shields the particle core from the electric field, so that the effect of changing ε_{core} becomes visible. The relaxation broadens with the emergence of a distinct second relaxation frequency as ε_{core} takes larger values. In Figure 5 it is shown that increasing ε_{matrix} has the effect of accentuating existing behavior; the shape of the frequency response observed in the case of $\varepsilon_{matrix} = 1$ is essentially repeated as ε_{matrix} increases, but with significantly increased values of ε' and ε'' due to increasing inter-particle capacitance. There is also a reduction in the lower relaxation frequency as ε_{matrix} increases, but no obvious change in the higher relaxation frequency. These observations are in qualitative agreement with findings of modelling studies on the optical properties of metallic nanoshells [33, 43].

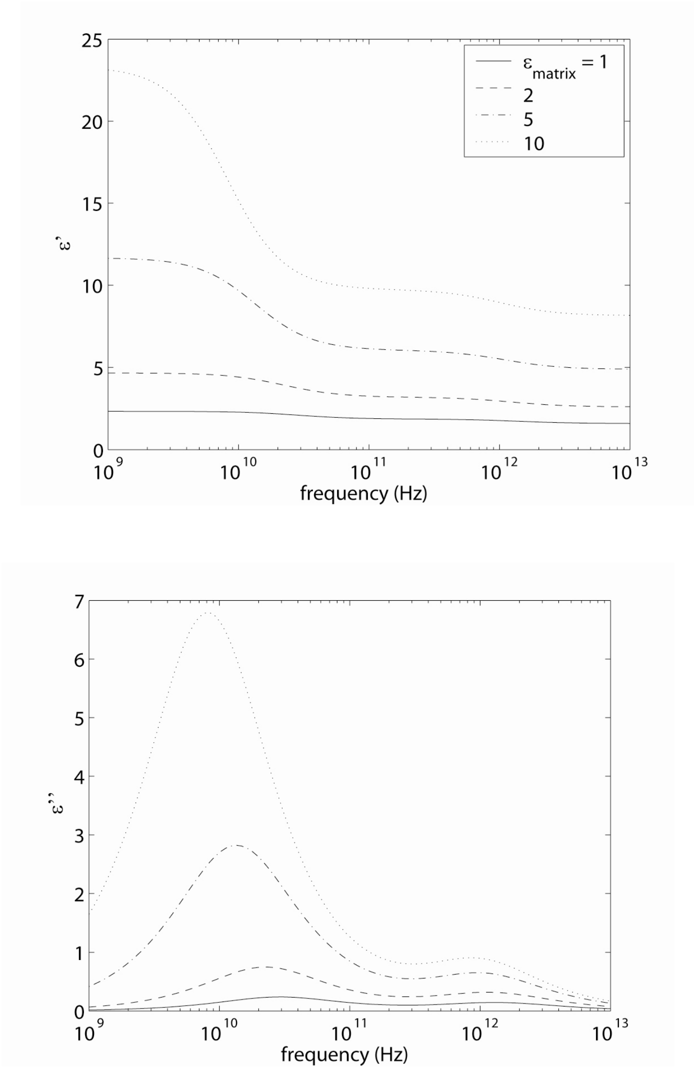

Figure 5. Real and imaginary parts of bulk permittivity for a composite material containing spherical filler particles, as a function of frequency and dielectric constant of the host medium, ε_{matrix}. $\varepsilon_{shell} = 1 + i100/(\omega\varepsilon_0)$ and $\varepsilon_{core} = 10$. $f = 0.3$.

The broader indication of results presented in this section is that dielectric relaxation due to interfacial polarization can be designed at arbitrary frequency, by suitable choice of materials.

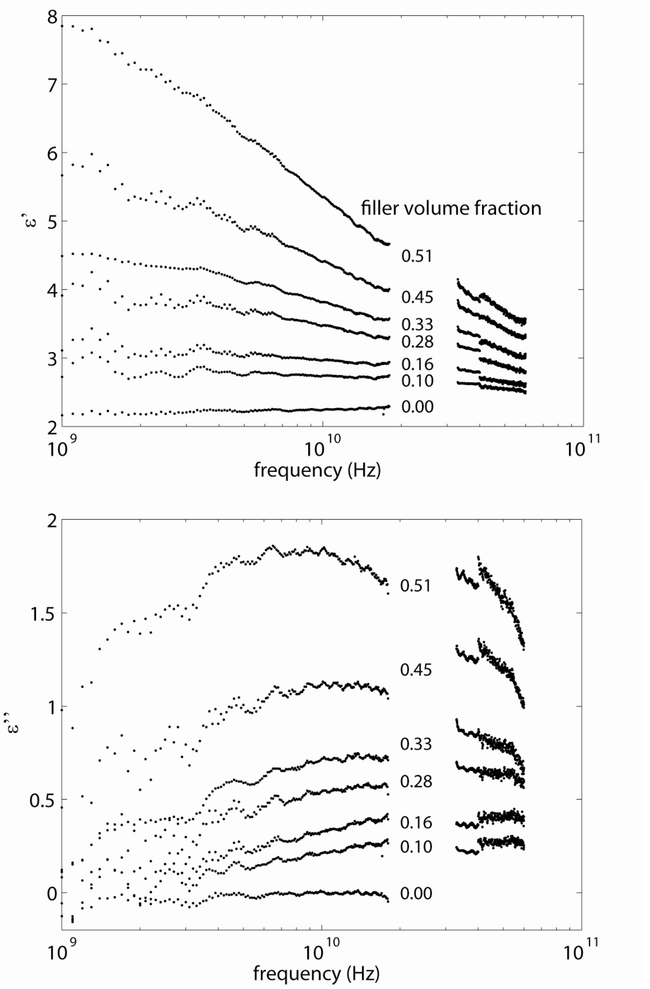

Figure 6. Relative permittivity of composite samples formed from tungsten-coated microbubbles in paraffin wax, for various values of filler volume fraction [19]. Mean filler particle radius is 15 μm and nominal tungsten thickness is 20 nm.

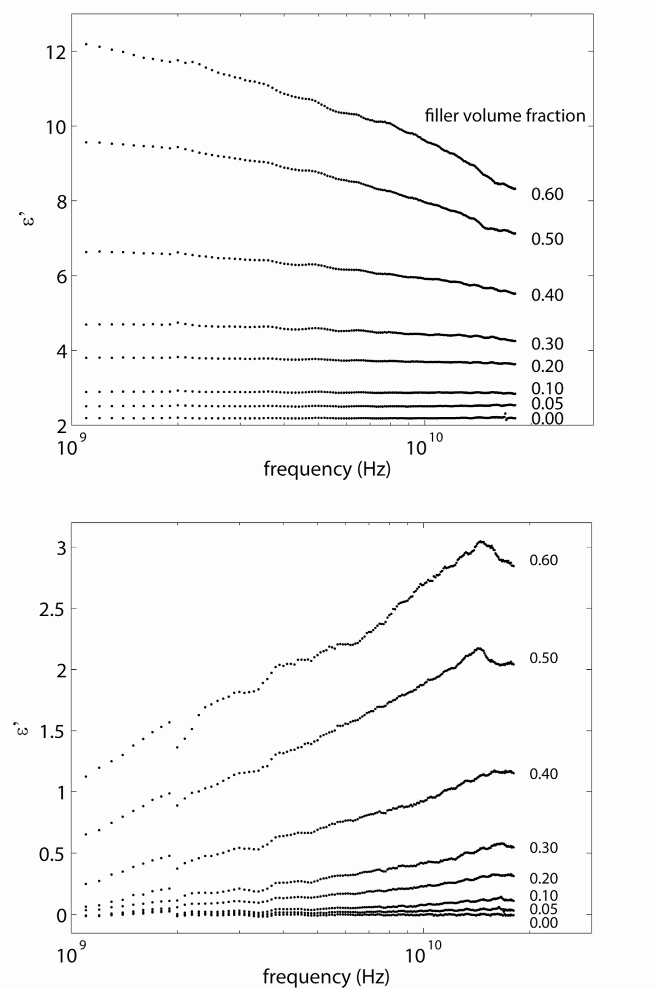

Figure 7. As for Figure 6 but for filler particles with mean radius 30 μm and nominal tungsten coating thickness 3 nm [47].

3 EXPERIMENTS

In practice, dielectric relaxation in the microwave frequency range has been observed for spherical filler particles with thin, discontinuous metal coatings [19, 46, 47]. Metal coatings a few nanometers thick exhibit significantly reduced conductivity compared to that for the bulk material, due to such factors as reduction of the electron mean-free-path and surface roughness of the coating [18]. Discontinuities in the coating also strongly reduce the effective coating conductivity [48]. In Figures 6 and 7, experimental measurements of bulk permittivity on composites formed from tungsten-coated glass microbubbles embedded in paraffin wax are shown [46, 47].

Results shown in Figure 6 are for filler particles with mean radius approximately 15 μm and nominal tungsten coating thickness 20 nm. Those shown in Figure 7 are for filler particles with mean radius approximately 30 μm and nominal tungsten coating thickness 3 nm. In both cases, a thin ($\approx$ 3 nm) outer coating of alumina on each particle acts to prevent percolative electrical conduction in the composite at higher filler volume fractions. In the frequency range under study, the alumina is otherwise passive in contributing to the bulk dielectric constant of the composite, as shown in reference [19] where the dielectric behavior of the composite was successfully modelled even when the alumina coating was ignored in the calculation. Measurements from 1 to 18 GHz were made using a 7 mm coaxial line transmission/reflection method. For results shown in Figure 6, higher frequency measurements were made using two rectangular waveguides. Mismatches between data sets taken with the three different types of sample holder are visible, but the trends are clear. The dielectric relaxation is particularly obvious for the higher-volume-fraction specimens in Figure 6 since, for these, υ_{rel} lies well within the range of experimental measurement ($\upsilon_{rel} \approx 10$ GHz for $f = 0.51$). From Figure 7 it appears that υ_{rel} for the sample with $f = 0.6$ is approximately 17 GHz or higher, since the sharpness of the peak is unlikely due to relaxation but may be due to resonance in the sample itself or may appear as a consequence of the sample/test geometry. While the mean values of t, equation (6), for these two systems ($t \approx 10^{-3}$ and 10^{-4}, calculated using nominal layer thickness values, for fillers in Figures 6 and 7 respectively) suggest that the relaxation frequency should be lower for the system of Figure 7 than for that of Figure 6, which is not the case, the explanation lies in the non-uniformity of the conductive coating. The tungsten coating is produced by sputter deposition and, in the case of the nominally thicker (≈ 20 nm) coatings, has been shown to be fairly uniform but discontinuous by means of scanning electron microscopy [23]. It is likely that similar discontinuities exist in the nominally thinner tungsten coating, which means that the parameter t is not properly defined for these systems and deductions based on its value cannot be made. The relaxations observed in Figures 6 and 7 are broad, and the dominant broadening mechanism is the distribution of coating conductivities due to variations in the coating uniformity, with a lesser contribution from polydispersity of the particles [19, 42, 49].

4 CONCLUSION

Dielectric relaxation, observed in measurements of relative permittivity of a composite material, can be tuned to a specific frequency by using filler particles with a conductive coating or shell. This tunable relaxation is due to entrapment of free charge at the interfaces in the system, leading to interfacial polarization. The frequency at which the relaxation occurs depends strongly on the properties of the conductive shell. For a uniform coating on spherical particles, the critical parameters are the conductivity of the coating and its thickness relative to the particle radius.

Experimental results shown here exhibit broad dielectric relaxations due to non-uniformity in the conductive coatings produced by sputter deposition. Chemical methods, by which conductive shells have been fabricated as fillers for tailoring optical properties of composite materials [49, 50], offer the possibility of tighter control on the radius, thickness and uniformity of conductive shell filler particles. Greater control in the fabrication of these fillers will permit their exploitation as more finely tuned absorbers of microwave radiation for various applications.

APPENDIX

In equation (3), the c_i are given by

$$c_1 = -\left[16\left(\frac{3}{4\pi}\right)^{10/3}\left(a'_{20}\right)^2\right] / \left[\frac{1}{L_3^{23}} + 20\left(\frac{3}{4\pi}\right)^{7/3} a'_{30} f^{7/3}\right], \tag{7}$$

$$c_2 = -176\left(\frac{3}{4\pi}\right)^{14/3} L_5^{23}\left(a'_{30}\right)^2, \tag{8}$$

where L_s^{23} is a coefficient obtained by applying continuity conditions on the electric potential at the surface of the filler particles. This is the interface between regions 2 and 3, shown in Figure 2. Explicitly,

$$L_s^{23} = \frac{1-\rho_{23} g_s}{\rho_{23} g_s + (s+1)/s}, \tag{9}$$

wherein

$$\rho_{ij} = \varepsilon_i / \varepsilon_j, \tag{10}$$

$$g_s = \frac{1 - [(s+1)/s](f_1/f)^{(2s+1)/3} L_s^{12}}{1 + (f_1/f)^{(2s+1)/3} L_s^{12}} \tag{11}$$

and L_s^{12} is a coefficient obtained by applying continuity conditions on the electric potential at the interface between the core and layer of the filler particles; regions 1 and 2 shown in Figure 2:

$$L_s^{12} = \frac{1-\rho_{12}}{\rho_{12} + (s+1)/s}. \tag{12}$$

The coefficients $a'_{nm} = l^{2n+1} a_{nm}$, where l is the side length of the unit cell of the simple-cubic lattice, arise in summing over an infinite number of lattice sites and have numeric value [51] $a_{20} = 3.108227$ and $a_{30} = 0.5733293$. The volume fraction of the particle core is f_1 whereas $f = f_1 + f_2$ is the volume fraction of the entire particle; core and layer together.

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