2004 Annual Report Conference on Electrical Insulation and Dielectric Phenomena

Dielectric relaxation of a composite with tungsten nano-layered spherical filler particles

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Abstract: The thickness and conductivity of a surface coating on filler particles in a composite material are critical parameters in controlling the frequency at which dielectric relaxation occurs. In this paper, experimental results are presented for composites formed from tungsten-coated glass microbubbles, embedded in a matrix of paraffin wax. The tungsten coating is of the order of 10 nm thick. There is an outer coating of alumina, a few nm thick, to prevent oxidation of the tungsten and to prevent the formation of conducting pathways in the composite. Dielectric relaxation is observed at around 10 GHz. A remarkable feature of the system is the way in which the relaxation frequency is shifted, by approximately six decades, from the calculated value for a similar composite formed with solid tungsten filler particles ($\approx 10^{16}$ Hz). This shift is attributed to the geometrical confinement of the conductor within a thin shell, and to the reduction in conductivity of the thin tungsten layer when compared with the conductivity of bulk tungsten.

Introduction

In a material composed of spherical, homogeneous, metallic filler particles dispersed in a non-conductive matrix, dielectric relaxation due to interfacial polarization of the conduction electrons occurs at approximately 10^{16} Hz, calculated according to the Maxwell-Wagner-Sillars (MWS) formula for dilute systems of nonagglomerating particles in which the interrogating wavelength is significantly larger than the length scale of variations in the composite microstructure [1]. In such systems, only dipole moments are induced since the local field acting on each particle is approximately uniform. Making the same assumptions for a system of spherical metallic shells dispersed in a non-conductive matrix, it is found that the frequency of MWS relaxation depends only on the ratio of the total particle radius to the core radius, and not on the absolute size [2]. Formulae for the relaxation frequencies observed in these systems with inhomogeneous, layered filler particles are given in [3]. In a case where the thickness of the metallic layer is about 0.1% of the particle radius, the relaxation frequency is shifted downwards in frequency by something over two decades, to approximately 10^{14} Hz [4], if the layer conductivity value remains the same as that of the bulk metal.

In this paper, the MWS relaxation of a material composed of spherical tungsten shells dispersed in paraffin wax is studied. MWS relaxation is observed at approximately 10 GHz, well below the values predicted by theory for a dilute dispersion of a) solid tungsten spheres and b) spherical tungsten shells in which the conductivity of the shell is assumed to be that of bulk tungsten. The additional downward shift in relaxation frequency is attributed to a significant reduction in the conductivity of the tungsten shell due to reduction of the mean free path of the conduction electrons in the thin tungsten layer.

Filler particles

The filler particles are formed by sputter deposition of tungsten onto hollow glass micro-spheres (3M Scotchlite™ S60 glass microbubbles) [5]. An additonal coating of alumina prevents oxidation of the tungsten and insulates against the formation of conducting pathways in the composite. This has the benefit that the interfacial polarisation process can be studied in isolation from conduction effects. The core particle mean radius is 15 μm, but there is significant variation about this mean, as seen in Figure 1.

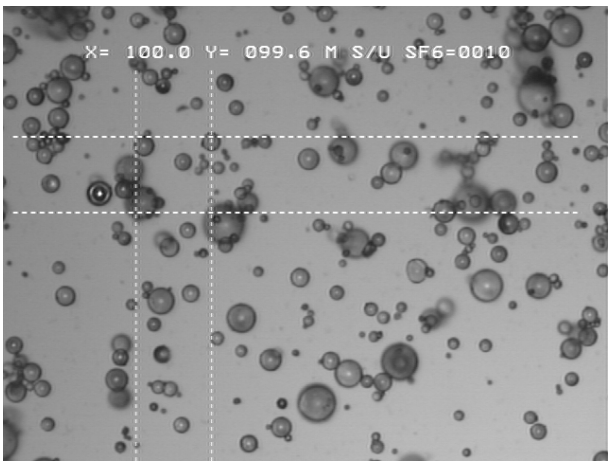

Figure 1: Micrograph showing the distribution in size of tungsten-coated microbubbles. The marked square is 100 μm x 100 μm.

The thickness of the tungsten layer is nominally 20 nm and the thickness of the protective coating of alumina is nominally 3 nm, although there is also variation about these mean values [6]. Some investigations suggest that the tungsten forms a continuous coating on the substrate micro-spheres, but that the surface is rough [6]. For some metals, on the other hand, it is known that for film thicknesses below about 40 nm the films exhibit a non-continuous 'island' structure [7]. The precise character of the metal coating is the subject of a future investigation.

Some physical properties of the particles are summarised in Table 1.

Table 1: Physical properties of tungsten-coated microbubbles.

Coated particle		**Source**
density (gcm^{-3})	0.54 ± 0.03	helium pycnometer
crush pressure (MPa)	69	[5]
Core particle		
mean radius (μm)	15	[8]
10^{th} centile radius (μm)	7.5	[8]
90^{th} centile radius (μm)	27.5	[8]
shell thickness (μm)	1.311	calculated
Mean coating thickness (nm)		
tungsten	20	[6]
alumina	3	[6]

Microwave frequency permittivity measurements

Method and results

Mixtures were prepared for filler volume fractions in the nominal range 0 to 0.55 by hand blending pre-weighed quantities of the two constituents on a hot plate at a temperature above the melting point of paraffin wax (approximately 60 ºC). Once the wax had melted the mixture was removed from the heat and mixing continued until solidification occurred. Samples were then formed by cold-pressing pellets of appropriate cross-sectional shape and dimension for measurements using 7mm coaxial, WG22 and WG24 rectangular waveguide sample holders. Pressures of approximately 63 ± 8 MPa (coaxial samples) and 58 ± 8 MPa (waveguide samples) were applied for 30 seconds using a KBr press. These pressures were chosen to expel as much trapped air as possible while not exceeding the crush pressure of the microbubbles (Table 1). Once the pellets had been made, their weight and thickness were measured using a five-place microbalance and calibrated micrometer, respectively.

It was observed that the value of filler volume fraction, f, calculated from i) the pre-weighed quantities of the two constituents in the mixtures and ii) the weight and volume of the samples, assuming known constituent densities, were different (Table 2). This is attributed to difficulty in achieving uniform mixing in small batches, resulting in likely variations in sample filler concentrations, even when taken from the same master batch. The quoted values are obtained by averaging.

Table 2: Filler volume fraction values.

nominal	mixture	sample	mean
0.10	0.11	0.08	0.10 ± 0.02
0.15	0.17	0.15	0.16 ± 0.01
0.25	0.27	0.28	0.28 ± 0.01
0.30	0.33	0.34	0.33 ± 0.01
0.40	0.43	0.47	0.45 ± 0.02
0.50	0.53	0.49	0.51 ± 0.02

The complex reflection and transmission coefficients of the samples were measured in various parts of the microwave frequency spectrum by placing them in a section of transmission line and measuring S-parameters, as described in [9]. A HP8510C vector network analyser with HP8515A S-parameter test set was used. Response in the frequency ranges 1 to 18, 33 to 40 and 40 to 60 GHz was measured using 7mm coaxial, WG22 and WG24 waveguide sample holders, respectively. The complex permittivity of the samples was then derived from the measured reflection and transmission coefficients according to the method described by Baker-Jarvis [10], with the assumption that the samples were non-magnetic. This assumption and method, where valid, reduces measurement uncertainties and improves loss resolution [11]. The results are shown in Figure 2.

Observation and interpretation

Clear evidence of MWS relaxation is observed in the measured frequency range. The peak in ε'' occurs at approximately 10 GHz for $f = 0.51$, shifting to higher frequency for smaller values of f, in qualitative agreement with theory [1,12]. The ripples observed in the data are due to residual mis-matches, after calibration, that lead to multiple reflections in the sample and sample cell.

For a particular value of f, systematic shifts in the values of ε' and ε'' are commonly observed between the frequency ranges corresponding to the different sample cells. This is attributed to small differences in pressure applied during sample fabrication, and to variations in filler dispersion, despite the fact that the same master batch was used to make samples for each of the three frequency ranges. Despite the presence of some discontinuities between the data sets, the bounding of the peak in ε'' is clear for $f = 0.28$ to 0.51. For values of f less than 0.28, further measurements at higher frequency are needed to properly observe the loss peak.

A theoretical study of this system, based on effective medium theory adapted for layered filler particles [2], finds that the relaxation frequency ν_{rel} observed experimentally is shifted lower, by several decades, than that predicted by theory. The relaxation is also significantly broader than predicted theoretically. The shift in ν_{rel} is likely explained by significant reduction in the mean-free-path of the conduction electrons in the thin tungsten coating, and the consequent reduction in conductivity. It may be the case that the tungsten coating is not continuous, since similar work on continuous gold nanoshells at optical frequencies does not observe a similarly large downward shift in ν_{rel} [13]. The broadening of the dielectric loss peak is attributed primarily to the existence of a distribution of metal coating thickness, and the consequent conductivity distribution. The distribution in particle radius plays a lesser role in broadening the loss peak. This interpretation is in line with observations on smaller (100 to 250 nm diameter) metal shells at optical frequencies [13], in which it is also pointed out that the shape of the loss peak can be explained in terms of classical electromagnetic theory, without recourse to quantum confinement effects.

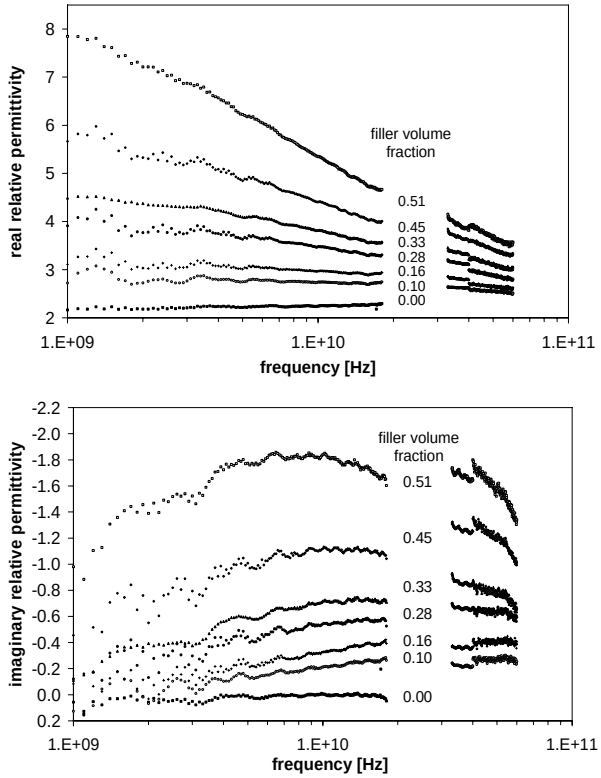

Figure 2: Relative permittivity of composite samples formed from tungsten-coated microbubbles in paraffin wax, for various values of filler volume fraction. Measurements were made using a HP8510C vector network analyzer, HP8515A S-parameter test set and 7mm coaxial, WG22 and WG24 transmission line sections.

Low frequency permittivity measurements

Method and results

Samples for permittivity measurements in the frequency range 10^{-4} to 10^{7} Hz were mixed in the same way as those for measurements made in the microwave frequency range, as described above. In this case, the pellets were cylindrical discs with diameter 10 mm, for use with a Novocontrol Alpha Dielectric Spectrometer, in which enhanced loss tangent resolution is obtained by means of an active sample head which eliminates sample lead noise. The electrodes on either side of the sample were formed by the application of silver-loaded conductive paint.

Measurements were made for samples with nominal filler volume fractions f = 0.1, 0.2, 0.3 and 0.5. The results are shown in Figure 3.

Observation and interpretation

The results shown in Figure 3 indicate that the conductivity of the composite increases with increasing filler concentration, but that the conductivity across the bulk material remains low ($\approx 10^{-10}$ S/cm) even as close-packing is approached. This shows that the presence of the outer coating of alumina on the filler particles is effective in preventing significant movement of charge carriers between filler particles. Charge transport across the bulk is evidenced by the appearance of a low frequency plateau in the conductivity. Samples f = 0.2a, 0.2c, 0.3 and 0.5 exhibit such a plateau, indicating that charges are able to hop or tunnel between adjacent filler particles, and that there exists a network of touching particles spanning the bulk of the material in these samples. It is interesting to note the different behavior of the three samples a, b and c, f = 0.2, at frequencies below 1 Hz. Two of the samples (a and c) exhibit conductive behavior whereas sample b does not. A probable explanation for this is that the percolation threshold for the composite occurs at $f \approx 0.2$ and, due to variations in microstructure between the three samples, a and c show conductivity due to the presence of a percolating network whereas sample b does not.

Conclusion and future work

A material composed of tungsten-coated microspheres dispersed in paraffin wax is observed to exhibit MWS relaxation at approximately 10 GHz. An outer coating of alumina on the microspheres prevents significant conduction in the composite even as close-packing is approached. The low observed value of ν_{rel}, when compared with the values for solid tungsten particles

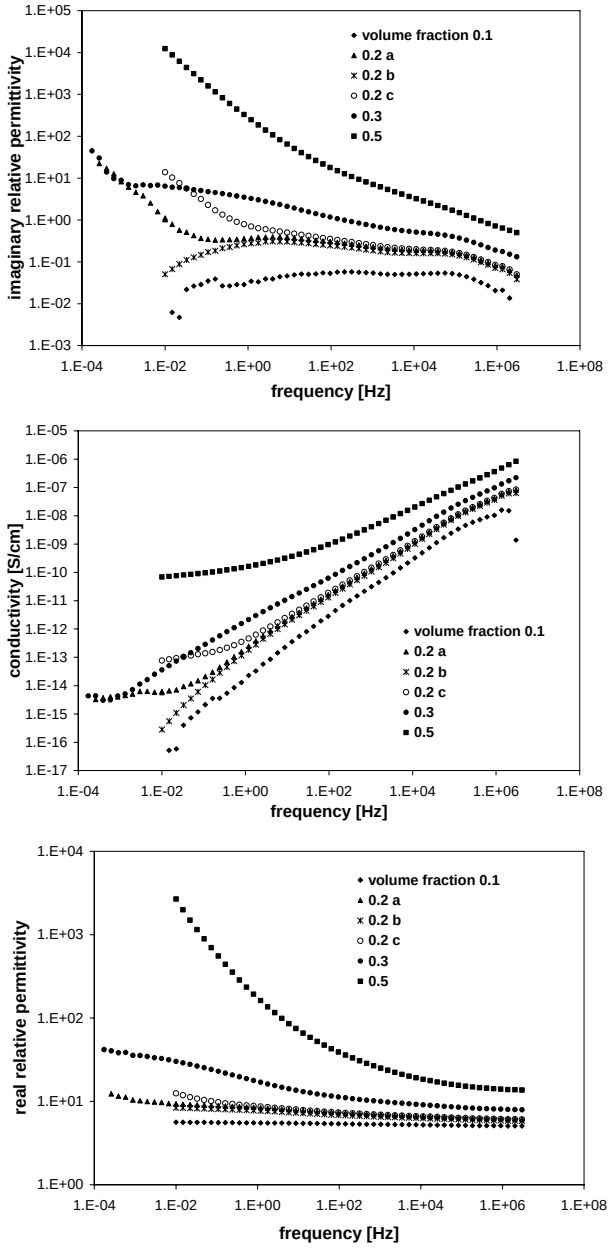

Figure 3: Relative permittivity and conductivity of composite samples formed from tungsten-coated microbubbles in paraffin wax, for various values of filler volume fraction. Measurements were made using a Novocontrol Alpha Dielectric Spectrometer**.**

(10^{16} Hz) and tungsten shells (10^{14} Hz), is supposedly due to reduced conductivity in the tungsten layer due to reduction in the mean free-path of the conduction electrons, perhaps due to discontinuities in the tungsten coating. Improved understanding of this system calls for closer examination of the thin tungsten film, for example by transmission electron microscopy, so that the conductivity can be determined from the physics of thin films. Proper understanding of the factors determining the film conductivity paves the way for model-based design of these types of materials with pre-specified absorption characteristics.

Acknowledgements

The authors gratefully acknowledge the supply of particles and related technical information by Dr. Craig Chamberlain of 3M, St.Paul, Minn., USA. This research was part-funded by the Ministry of Defence as part of the Corporate Research Programme. © QinetiQ limited 2004. N Bowler's work was performed at the Center for NDE at Iowa State University with funding from the Air Force Research Laboratory through S&K Technologies, Inc. on delivery order number 5007-IOWA-001 of the prime contract F09650-00-D-0018.

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