

Which Parameters Control Maxwell-Wagner-Sillars Relaxation? A Finite-Element Study of Carbon-Coated Silica / Epoxy Nanocomposites

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Abstract

Interfaces exhibiting Maxwell-Wagner-Sillars polarization are mainly due to the differences in the electrical properties among the different materials at the interfaces. Most of the high-permittivity polymer nanocomposites have this type of interfacing as their basic idea for extracting high dielectric constants. Though the characteristic peak corresponding to interfacial polarization is not usually found in the measured spectra of such materials. The relaxation related to the Maxwell-Wagner-Sillars (MWS) polarization remains invisible. With the help of a three-dimensional finite-element frequency-domain model of the DGEBA epoxy embedding carbon-coated silica ($\text{SiO}_2@\text{C}$) particles it was possible to figure out how varying different geometric and compositional features affects the behavior of the Maxwell-Wagner-Sillars (MWS) polarizations. Seventeen representative volume elements in different combinations of filler concentration (2.5-20 vol%), silica core diameter (35-100 nm) and carbon shell thickness (5-25 nm) were calculated over twelve decades (1 mHz - 1 GHz), resulting in 1337 convergent solutions. With 20 vol% filler concentration, the maximum permittivity increase was +75.6%, $\epsilon' =$ from 3.60 to 6.32. The calculated results were only off from the Maxwell-Garnett results for a perfectly conducting inclusion by 0.34%. Permittivity enhancement was practically independent of the core diameter and carbon shell thickness at a precision level of 2 ppm: loading alone sets the magnitude of the MWS contribution. Relaxation frequency recovered parameter-free from low-frequency Debye flank ranges from 23.1 to 70.5 GHz, and its value relies on the geometric features only through a parameter $\beta = (a/b)^3$ (the dimensionless core-to-particle volume ratio); identical spectra were obtained for two different cell designs with $\beta = 0.4705$ with precision greater than 0.01 ppm. The load affects the shift of the relaxation frequency over the entire range only by a very small magnitude of -15.8%. No tunable parameter (core diameter or shell thickness or loading) brings f_{MW} within measurable bands. Changing the filler architecture rather than its dimensions should be done if one seeks for better performance of the Maxwell-Wagner-Sillars polarization in high-permittivity polymer nanocomposite materials.

Keywords: Maxwell-Wagner-Sillars polarization, core-shell nanocomposites, dielectric relaxation, impedance spectroscopy, effective medium theory.

1. Introduction

Adding conductive or high-permittivity filler into the matrix to obtain polymer nanocomposites is a popular way to have a dielectric with low loss factor (dissipation factor) and still be able to possess high permittivity, which is necessary for energy storage and low-loss substrates used in millimetre-wave/sub-terahertz electronics [1-3]. The increase in permittivity in polymer nanocomposites is commonly ascribed to Maxwell-Wagner-Sillars (interfacial) polarization [4-6]. Maxwell-Wagner-Sillars (MWS) polarization is the polarization that occurs whenever two materials with dissimilar ratios of conductivity to permittivity meet at an interface. When an electric field is applied across the composite film a charge separation will occur across the interface between the two phases so that the normal component of the current density must stay continuous while that of the electric displacement need not, and the mismatch is taken up by free charge at the interface.

Because the change in the displacement will lead to the free charge getting concentrated in the region where the interface is, that means the surface will have a very large induced dipole [7]. The size of the dipole depends on the volume of the particle rather than simply on the polarization property of the molecules involved [8]. This dipole is what causes the effective permittivity to be higher than the mere volume averaged contribution of the components of the composite.

Yet, as free charges have to be conducted to the surface, polarization can only be a relaxation type of process which means that it comes with relaxation time. So, the polarization cannot follow the field indefinitely: it is a relaxation process, described in the simplest case by a Debye response with a single time constant [4,9]. Two consequences follow: Below the relaxation frequency the polarization is fully developed and contributes its entire static increment to ϵ' while dissipating almost nothing; above it the increment is lost. The relaxation frequency therefore bounds the useful operating band. It is also the only unambiguous signature of the mechanism, a loss peak in ϵ'' with a step in ϵ' , so in its absence an observed permittivity gain is consistent with interfacial polarization but is not evidence of it.

For a single spherical inclusion of complex permittivity ϵ_p^* inside a matrix ϵ_m^* , the interfacial relaxation time is [4,9]

$$\tau = \epsilon_0 (2\epsilon_m + \epsilon_p) / (2\sigma_m + \sigma_p) \quad (1)$$

where, σ_p is the conductivity of the spherical inclusion and σ_m is the conductivity of the matrix, and which shows what could move it: the permittivities and conductivities of the two phases, and the internal geometry of the inclusion through ϵ_p and σ_p for a structured particle. Filler loading enters separately, through the effective-medium relation that couples the single-particle response to the composite.

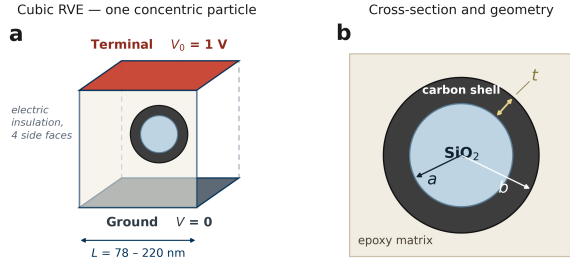


Fig. 1. One coated sphere per cubic cell; L set by ϕ , so loading is exact.

In earlier works, the complementary architecture has been modeled in a finite element study, presented at the ACerS Annual Spring Meeting [10]. That model featured carbon black cores with thin insulating SiO_2 coatings, randomly dispersed in epoxy. The previous study showed that changing filler concentration modifies the effective permittivity, and an insulating coating suppresses the formation of a continuous ohmic pathway at high concentrations of filler. This previous work focused only on the field distribution in the quasi-static regime and did not deal with the relaxation dynamics. The material produced by the method used here, Stöber silica, hydrothermally carbon-coated and pyrolyzed, is the opposite structure, a silica core that is insulating with a conductive carbon shell written at $\text{SiO}_2@\text{C}$. Broadband dielectric measurements on the composites in this research reproduce the increase in permittivity with filler loading but do not show a loss peak nor a step in ϵ' anywhere within the frequency range available. This study looks for whether the MWS mechanism is actually absent or outside our measurement band, and if the latter, which parameters, if any, might be able to visualize it.

2. Numerical Model

2.1 Governing equations

The composite is treated as a linear, isotropic, quasi-static conductor-dielectric. Charge conservation in the frequency domain requires

$$\nabla \cdot \mathbf{J} = 0, \quad \mathbf{J} = (\sigma + j\omega\epsilon_0\epsilon_r) \mathbf{E}, \quad \mathbf{E} = -\nabla V \quad (2)$$

with σ the electrical conductivity, ϵ_r the relative permittivity, $\omega = 2\pi f$, and V the electric potential. In order to solve Equation (2), we employed the Electric Currents interface on COMSOL Multiphysics 6.2 for the Frequency Domain analysis [11]. Each phase was assigned a real σ and ϵ_r , thereby frequency dispersion in the result was entirely caused by the geometry and not by the material properties.

The complex impedance of the cell was obtained from the terminal quantities, $Z^*(\omega) = V_0 / I_0$, and converted to an effective complex permittivity through the vacuum capacitance of the cell, $C_0 = \epsilon_0 L$:

$$\epsilon^*(\omega) = \epsilon' + j\epsilon'' = [j\omega Z^*(\omega) C_0]^{-1} \quad (3) \quad [12]$$

so ϵ' , ϵ'' and $\tan \delta = \epsilon''/\epsilon'$ come from the same solution that produces the impedance spectrum, and simulation and measurement can be compared in either representation.

2.2 Geometry and representative volume element

A single concentric core-shell sphere was placed at the centre of a cubic representative volume element (RVE), shown in Fig. 1. The silica core has radius $a = d/2$ and the carbon shell, which has a thickness t , and outer radius $b = a + t$, so the coated particle diameter is $d_p = d + 2t$. The cube edge is set by the target volume fraction ϕ ,

$$L = d_p (\pi / 6\phi)^{1/3} \quad (4)$$

which fixes ϕ exactly and allows core diameter and shell thickness to be swept at constant loading across the seventeen cases L ranges from 78 to 220 nm. As ϕ and not L is held fixed, the absolute impedance of the cell is not comparable between cases. All cross-case comparisons are therefore made on $\epsilon^*(\omega)$, on normalized impedance, or on characteristic frequencies, none of which carry the cell dimension.

Two dimensionless quantities describe the particle and are used throughout:

$$\beta = (a/b)^3, \quad \phi = (\pi/6) d_p^3 / L^3 \quad (5)$$

β is the fraction of the coated particle occupied by the insulating core; $\beta \rightarrow 1$ is a vanishingly thin shell and $\beta \rightarrow 0$ a solid carbon sphere.

2.3 Material properties and boundary conditions

Phase properties are found in Table 1. The carbon shell conductivity is the value confirmed for pyrolyzed carbon during validation. The value for shell's permittivity was taken from literature, and the results are insensitive to it (Section 4.5). Also, epoxy that has been hardened is not a completely perfect insulator, so, when a carbon shell is completely wrapped up in silica and epoxy, it turns into an electrically floating conductor as displacement currents will disappear at a low frequency, practically making the system matrix highly singular. By assigning a small but realistic leakage conductivity to the matrix, a conduction road to the electrodes is recovered and the computation converges down to 1 mHz. The conductivity used, $1 \times 10^{-8} \text{ S m}^{-1}$, is a modelling assumption with a real effect on the simulated low frequency ϵ'' and on the impedance corner frequency, which has been reported as such.

Table 1. Phase properties used in all simulations.

Phase	ϵ_r	$\sigma \text{ (S m}^{-1}\text{)}$
SiO_2 core	3.9	1×10^{-14}
Carbon shell	12	1×10^2
DGEBA-DETA epoxy	3.6	1×10^{-8}

A Terminal (Voltage = $V_0 = 1 \text{ V}$) was attached to the $+z$ face of the cube and Ground to the $-z$ face; the four lateral faces remain with the default electric-insulation condition. The domains were divided into free tetrahedra

and the mesh was densified along the shell so that its thickness was represented by at least two elements. The frequency sweep starts at 1 mHz and ends at 1 GHz. To achieve a good convergence considering the large difference in conductivity (sixteen orders of magnitude between carbon and silica), the direct PARDISO solver with a high relative tolerance of 0.01 was necessary.

2.4 Parametric study

Three sweeps were performed where each time only one variable was changed at a time (Table 2). This has resulted in seventeen distinctive RVEs and 1337 solution points that have converged. In this case changing just one parameter at a time is enough because the two geometric parameters actually work through one single combined parameter.

Table 2. Parametric sweeps. All cases were solved from 1 mHz to 1 GHz.

Sweep	Variable	Levels	Held fixed
S1	ϕ	2.5-20 vol% (8)	$d = 70$ nm, $t = 5$ nm
S2	d	35, 50, 70, 100 nm	$\phi = 10$ vol%, $t = 5$ nm
S3	t	5, 10, 15, 20, 25 nm	$\phi = 10$ vol%, $d = 70$ nm

2.5 Validation

Before interpreting the 3D results, the entire modeling chain, from generating geometry through to defining materials, setting up boundary conditions, carrying out meshing and extracting impedances, was first checked for accuracy. This was done by comparing the results with those obtained from the exact expression for the dilute dispersion of coated spheres. The equivalent complex permittivity of one coated sphere (core ϵ_1^* , shell ϵ_2^*) is [13],

$$\epsilon_p^* = \epsilon_2^* [(\epsilon_1^* + 2\epsilon_2^*) + 2\beta(\epsilon_1^* - \epsilon_2^*)] / [(\epsilon_1^* + 2\epsilon_2^*) - \beta(\epsilon_1^* - \epsilon_2^*)] \quad (6)$$

and the Maxwell-Garnett effective medium for a volume fraction ϕ of such particles in a host ϵ_m^* is

$$\epsilon_{\text{eff}}^* = \epsilon_m^* [\epsilon_p^* + 2\epsilon_m^* + 2\phi(\epsilon_p^* - \epsilon_m^*)] / [\epsilon_p^* + 2\epsilon_m^* - \phi(\epsilon_p^* - \epsilon_m^*)] \quad (7)$$

with every phase entered as $\epsilon_r^* = \epsilon_r - j\sigma/(\omega\epsilon_0)$. At the $\phi = 0.0126$ 2D axisymmetric cell, the computed ϵ' value of 3.7377 proved to be a very accurate four digits match to the analytical solution (3.7378) and the computed value of ϵ'' differed from the analytical value by no more than 0.8% at all frequencies over the ten decades. Equations (6) and (7) once more appear in Section 4 as a mean of interpretation and never as a function to be fitted: they do not involve any freely varying parameters.

2.6 Extraction of the relaxation frequency

Frequency response was simulated up to 1 GHz, which proves to be below the relaxation (Section 3.2). The relaxation was therefore located from its low-frequency flank without fitting. For a Debye process, $\epsilon^*(\omega) = \epsilon_\infty + \Delta\epsilon/(1 + j\omega\tau)$, the limit $\omega\tau \ll 1$ gives $\epsilon'' \approx \Delta\epsilon \omega\tau$ and $\epsilon_s - \epsilon' \approx \Delta\epsilon (\omega\tau)^2$, so that at any frequency f on that flank,

$$f_{\text{MW}} = 1/(2\pi\tau) = f \cdot \epsilon''(f) / [\epsilon_s - \epsilon'(f)], \quad \Delta\epsilon = \epsilon''(f) f_{\text{MW}} / f \quad (8)$$

At the highest computed frequency, both parameters were evaluated, with ϵ_s being considered as the median of ϵ' over the 1 kHz to 1 MHz range. At 1 GHz the conduction contribution accounts merely for 2.4×10^{-7} out of ϵ'' , which is five orders below the interfacial term and, because of this, no subtraction is needed. It is observed that these values are in close agreement with separate estimation by equations (6)-(7) within the limit of 1% for seventeen examples; so, we can infer that this extrapolation reflects the true nature of solution and not some kind of the method artifact.

3. Results

3.1 Origin of the permittivity enhancement

The effective permittivity of the material increases monotonically, from 3.60 for pure epoxy to 6.32 at 20 vol% with a 75.6% increase (as shown in Fig. 2a). The relation is superlinear in ϕ and is reproduced, with no free parameters, by the Maxwell-Garnett formula used for a perfectly conducting filler,

$$\epsilon_{\text{eff}} = \epsilon_m (1 + 2\phi) / (1 - \phi) \quad (9)$$

The deviation of the simulation result from theory is a very small one - less than 0.02% for volumes up to 10% and at 0.34% when the volume is at 20%. Such is the typical behavior of the difference between a periodic array and the dilute effective-medium assumption at higher concentrations that one can expect no better result from Eq. (9) (Figure 2b).

Evaluating the formula at work on bare silica spheres, assuming that the dielectric constant ϵ was 3.9 in that case, would be forecasting an increase of only 1.6% at 20 volumes percent. The silica core contributes almost nothing, so the whole enhancement is coming from conductive carbon shell. This is the quantitative way of saying that the gain comes from the interface, that shell conductivity (10^2 S m^{-1}) exceeds the shell's own displacement conductivity $\omega\epsilon_0\epsilon_r$ by three to fifteen orders of magnitude across the computed band. Because of this, each particle behaves like an equipotential body and Eq. (9) is exactly what one would get from a fully relaxed model i.e. at the low-frequency limit of the Maxwell-Wagner polarization.

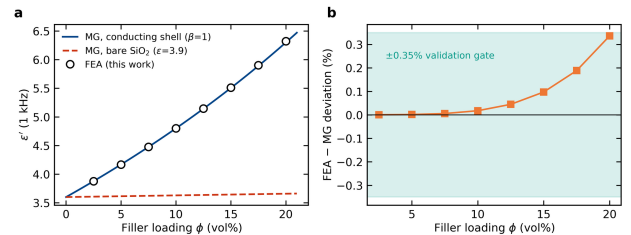


Figure 2. Permittivity enhancement and model validation. (a) ϵ' at 1 kHz against filler loading, with the Maxwell-Garnett limits for a perfectly conducting inclusion and for bare silica; (b) deviation of the finite-element result from Eq. (9). The silica core accounts for 1.6 percentage points of the 75.6% gain; the conductive shell supplies the rest.

3.2 The relaxation lies above the computed band

Fig. 3a displays $\epsilon'(f)$ for the eight loading levels. Each graph is nearly flat to within 0.05% across a span of twelve decades; there are no step and no dispersion seen in the entire interval from 1 mHz to 1 GHz. In Fig. 3b, the loss spectrum reveals this to be the underlying explanation. Below 2.5 MHz, the slope of ϵ'' is precisely -1.000 on a log-log plot, the hallmark of DC conduction, $\epsilon'' = \sigma_{\text{eff}}/(\omega\epsilon_0)$. Starting from the minimum at 2.5 MHz ($\epsilon'' = 1.8 \times 10^{-4}$ at 10 vol%) a second branch is formed with slope +0.98. Two different processes overlap

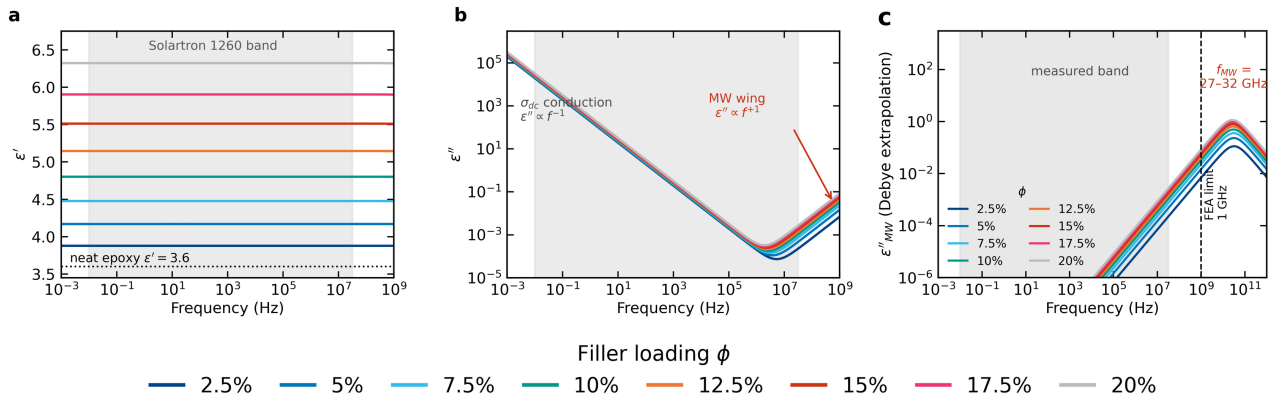


Figure 3. Dielectric spectra for all eight loadings. (a) ϵ' against frequency, flat to within 0.05% over twelve decades; (b) ϵ'' , showing the σ_{dc} conduction branch of slope -1 crossing the +1 flank of the Maxwell-Wagner process at 2.5 MHz; (c) the peaks reconstructed from that flank through Eq. (8), with apexes at ~27-32 GHz. Shading marks the practically available and usable measurement band.

3.3 Geometry does not change the magnitude of the response

By holding the load level fixed and varying the core diameter up to a $2.9\times$ factor and the shell thickness up to a $5\times$ factor, the relative permittivity ϵ' remains essentially the same at 4.8009 as plotted in Fig. 4a. The most extreme divergence among the nine shapes is only 2.1 ppm, a variation that equals the mesh discretization error. Like that, loss tangent at 1 kHz is steady at 0.04993 to within 0.002%, while the extracted DC conductivity varies by less than 0.02%.

This explanation follows directly from the equipotential condition discussed in Section 3.1. The outer surface of a body being an equipotential means that such a body, regardless of other parameters, only alters the external field with its volume. Since Equation (9) carries neither a length scale nor any internal structural parameters, the outcome is independent from the relative distribution of the volume between core and shell. That means, the unavoidable presence of particles having different diameters and thicknesses produced by wet-chemical synthesis does not influence the permittivity. This also means still none of the geometric tuning is able to raise the permittivity.

here. The conduction tail is on the left side and on the right side the low-frequency edge of a Debye peak which extends into the apex beyond the range of this calculation.

The usage of Eq. (8) in calculating that branch results in the placement of an apex at 30.3 GHz for the 10 vol% baseline geometry. In all of the seventeen cases, it was found the peaks are between 23.1 and 70.5 GHz. Reconstructed peaks are portrayed in Fig. 3c. The relaxation strength increases almost ten times, from $\Delta\epsilon = 0.223$ at 2.5 vol% to $\Delta\epsilon = 2.272$ at 20 vol%, while the underlying ϵ_∞ moves only from 3.65 to 4.05.

At frequencies below f_{MW} the interfacial polarization mechanism offers the full static increment while dissipating almost nothing. In the absence of a direct measurement technique, both fingerprints sit three to four decades above the highest frequency the available instrumentation reaches.

3.4 Geometry sets the timescale, through a single dimensionless ratio

Unlike the magnitude, the relaxation frequency is influenced by the geometry. For instance, keeping shell thickness fixed at $t = 5$ nm, and varying core diameter from $d = 35$ nm up to $d = 100$ nm brings the lowering of relaxation frequency from approximately 47.4 GHz to 23.1 GHz which corresponds to a ratio of lowering 2.05; Also increasing the shell thickness from 5 to 25 nm with the fixed diameter of the core of 70 nm causes the frequency to rise from ~30.3 to 70.5 GHz, this way the ratio is 2.33. One sweep lowers the frequency while the other increases it, and both results match the predictions of the single parameter β .

At the conducting limit, Eq. (6) changes into an effective particle conductivity

$$\sigma_p = \sigma_c \cdot 2(1 - \beta) / (2 + \beta) \quad (10)$$

which, together with the corresponding $\epsilon_p(\beta)$, determines τ through Eq. (1). Neither formula contains a fixed-length quantity: charging at the interfaces is only due to the time constant RC of the particle, it is not a time it would take to spread a given distance, for example.

In other words, the model prediction is that f_{MW} solely depends on β and that means with the same β value two particles of even different sizes would show the same

relaxation behavior. The simulations confirm it. The case $d = 35$ nm, $t = 5$ nm and the case $d = 70$ nm, $t = 10$ nm they share $\beta = 0.4705$ and are apart from being a two-fold difference of the particle diameter (45 versus 90 nm) and in RVE edge (78 versus 156 nm); and these models are developed, meshed and solved as independent models in separate sweeps. The relaxation frequencies obtained are 47.3812, 47.3812 GHz; and the relaxation strengths are respectively 0.88659 & 0.88659; the two ϵ' spectra across 41 calculated frequencies coinciding with each other to an accuracy of 0.01 ppm and the two ϵ'' spectra differ by 0.008%, at most. Figure 4c overlays two different geometric designs of particle shape onto one single β .

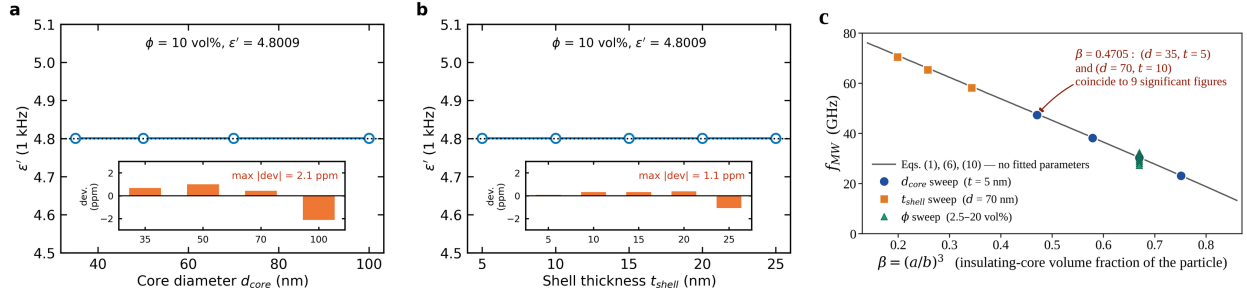


Figure 4. Geometry controls the timescale but not the magnitude. (a, b) ϵ' at 10 vol% against core diameter and shell thickness, invariant to 2.1 ppm (insets, parts per million); (c) f_{MW} for both geometric sweeps against $\beta = (a/b)^3$, collapsing onto the single curve predicted by Eqs. (1), (6) and (10) with no fitted parameters. The loading sweep is shown at its fixed β for comparison. The two cases at $\beta = 0.4705$, ($d = 35$, $t = 5$) and ($d = 70$, $t = 10$), coincide to nine significant figures despite differing twofold in absolute size.

3.5 The impedance representation

Recast as complex impedance, which is the form the measurement actually returns, the same solutions give an independent view of the result. All the seventeen instances result in one nearly ideal Debye semicircle in the Nyquist plot, after normalization by DC resistance: the depression angle of this circle-fit arc is less than 0.07° . There is no second loop and there is no constant-phase-element (CPE) character (Fig. 5a). This means that only one-time constant controls the entire measurable frequency range.

The intercept of the impedance semicircle with the real axis f_c of the semicircle is same ~ 49.9 Hz for each and every configuration, different loadings, different core diameters, and different shell thicknesses, because,

$$f_c = \sigma_{dc} / (2\pi\epsilon_0\epsilon') \quad (11)$$

this is explained by the finding of the work that σ_{dc} and ϵ' values are changed by the identical factor which eventually cancels. Although DC resistance of the cells varies from 360 to 960 TΩ respectively, it varies entirely as $1/(\sigma_{dc}L)$: a cell-size effect that carries no dielectric information, which is why the normalized representation is more meaningful [15].

Filler loading has marginal impact at this level. f_{MW} drops from 32.3 to 27.2 GHz through the 2.5-20 vol% loading range, by only $\sim 15.8\%$, without threshold or plateau, and it does almost nothing. The trend continues the acceleration: the local sensitivity $\partial f_{MW}/\partial \phi$ steepens monotonically from ~ 26.9 to ~ 32.3 GHz per unit volume fraction in the whole loading range. Every loading trend is characterized by the same nature - ϵ' , $\Delta\epsilon$ and σ_{dc} are superlinear in ϕ , and tan delta of 1 GHz comes to be linear to within 7%. The range simulated doesn't show any saturation. Loading determines how much interfacial polarization one gets while beta is how fast that polarization responds.

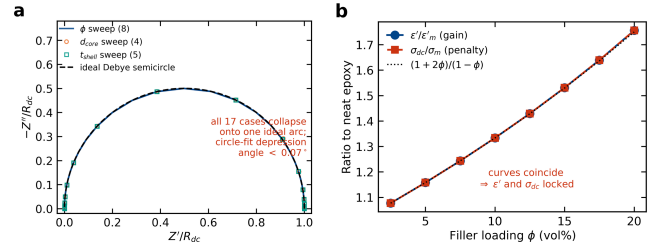


Figure 5. Impedance response and the permittivity-leakage coupling. (a) All seventeen cases normalized to R_{dc} collapse onto one ideal Debye semicircle (circle-fit depression angle $< 0.07^\circ$), with the intercept of the impedance semicircle with the real axis is fixed at 49.9 Hz; (b) permittivity gain and DC-conductivity penalty against loading, coincident with $(1 + 2\phi)/(1 - \phi)$ to better than 5×10^{-5} .

4. Discussion

4.1 What controls what

Table 3 presents the outcome of our parameter experiment. If we reframe it as a reply to the article title question that the size of the MWS response depends solely on filler loading while timescales are mainly determined by core-to-particle volume ratio β , to which filler loading contributes slightly, then you get the full picture. The two parameters are almost independent, which is convenient for design, but neither offers a useful enough range for the present purpose.

Table 3. Effect of each parameter on the MWS response. Ranges are over the full sweep; ϵ' and $\tan \delta$ at 1 kHz.

Quantity	ϕ : 2.5→20%	d: 35→100 nm	t: 5→25 nm
ϵ'	3.88 → 6.32	< 2.1 ppm	< 1.1 ppm
$\Delta\epsilon$	0.223 → 2.272	0.887 → 1.024	0.982 → 0.775
f_{MW} (GHz)	32.3 → 27.2	47.4 → 23.1	30.3 → 70.5
$\tan \delta$	0.04993 (fixed)	0.04993 (fixed)	0.04993 (fixed)
f_c (Hz)	49.9 (fixed)	49.9 (fixed)	49.9 (fixed)

Covered frequency range of f_{MW} for all simulated cases is about 23.1-70.5 GHz, a factor of 3.05. Upper band edge of measurement is 32 MHz. This means that the lower frequency relaxation is higher by a factor of 720, and to close that gap without changing shape (only would be a requirement for $\beta \rightarrow 1$), would require a shell with nearly no thickness, leaving no conductive path behind that caused the effect.

4.2 Permittivity and leakage are the same field problem

A second limitation comes from the loading sweep, and it is the one affecting the application more profoundly. DC conductivity of the composite is increased by 75.6% over that of neat epoxy at 20 vol%, the exact same number as the permittivity gain up to 3×10^{-5} (Fig. 5b). Such similarity is no accident and actually, the deviation is observed to be less than 5×10^{-5} for every loading: since both σ and ϵ' in DC limit satisfy the same Laplace equations and the same boundary conditions, an inclusion with the equipotential surface is an equipotential in both cases only so that they are both multiplied by an identical geometric factor from Eq. (9).

This has serious implications in practice. The loss tangent at 1 kHz is 0.04993 at all loadings and all geometry, that means any material performance metric which divides permittivity by leakage will be identically unity: the permittivity gained by adding filler is exactly offset by the leakage it introduces. It is also for this reason that the impedance corner frequency specified in Eq. (11) never changes. A conductive shell as a bare layer can't do anything different because a single mechanism is responsible for both material properties.

4.3 Why an outer silica layer addresses both problems

A relaxation fixed three decades too high and a permittivity gain that is limited to a leakage penalty, are a result of one thing: the conductive carbon shell is DC-connected to its surroundings through the matrix. One structural modification, addition of an insulating layer making outer layer resulting in $\text{SiO}_2@\text{C}@\text{SiO}_2$, will not only address both problems, and for the same reason. The carbon shell continues to polarize under AC, and most of the ϵ' gain is still there; but the leakage path is stopped because a series insulator is basically not passing through DC. In addition, this very same series element is responsible for the longer charging time constant of the interface resulting in an extra downward shift in the relaxation down. Using Eqs. (6), (7) to

double-shell particles gives a quantitative estimate, the condition being made though that this is an extrapolation based on a model already validated. At a particle size of $d=70$ nm, with a thickness of $t=5$ nm, an outer layer of SiO_2 of 0.5-10 nm, will lower the composite conductivity at DC from 1.333×10^{-8} to $8.57 \times 10^{-9} \text{ Sm}^{-1}$, exactly coinciding with the Maxwell-Garnett (MG) result for insulating (non-conducting) inclusions, i.e. $\sigma_m(1 - \phi)/(1 + \phi/2)$, and even less conductivity than the unfilled matrix itself (matrix conductivity at $\phi=0$).

The 30 GHz intrinsic process of the particle remains the same, and a much stronger second interfacial relaxation is predicted at 1-20 Hz, with $\Delta\epsilon$ varying from 2 to 62 given the outer layer thickness: charging of outer SiO_2 capacitance takes place now through the matrix, and the conductivity of the matrix is ten orders lesser than that of the carbon. The exact location or "position", as far as the frequency of this new relaxation, of course is not fixed. It depends linearly on the conductivity of the matrix. First of two predictions is that the conductivity of the composite DC should decrease to the level of insulated inclusions, a reduction by the factor $(1 - \phi)^2/[(1 + 2\phi)(1 + \phi/2)]$. Second prediction, which is directly verifiable, is that the impedance of the corner frequency should decrease from 49.9 Hz to 32-37Hz at 10 vol%, given the thickness of the overlayer, a decrease of 26-35% that is independent of the matrix conductivity assumed. Actually, this "corner frequency" has remained the same or constant among all seventeen cases analyzed.

4.4 Consequences for characterization

The findings change how an experiment may be conducted. Since Eq. (10) is linear in σ_c , a reduction by four orders is going to bring relaxation frequency close to 3 MHz which is fully in range of the measured frequencies. It may be a valid way of looking at it, but the application is different: in order for the substrate to work at millimeter-wave frequencies, the relaxation should be above the operating frequencies, otherwise, the permittivity gain is not available there at all. The invisibility of relaxation is commonly present in a well-functioning high-frequency dielectric material, that means, checking out the mechanism on an engineered model system with very high relaxation time is preferable to the material that will actually be in service.

4.5 Limitations

The model simulates the system with only one particle inside each periodic cell having insulated lateral boundaries, so this is a case of an ordered non-percolating dispersion; agglomeration, particle-particle field overlap, and percolation are outside the scope of the model. A previous study [10] indicates that such effects are quite significant above roughly 15% vol.%. The dielectric constant of the carbon shell is used as a placeholder, while though, it appears only through ϵ in Eq. (1) and if the dielectric constant is changed by a factor of two then the relaxation frequency f_{MW} changes by less than 20% while ϵ' remains unchanged. In fact, none of the conclusions of this work depend on it. The

matrix leakage conductivity is a model parameter that directly determines f_c and the low frequency ϵ'' , though not $\epsilon'\Delta\epsilon$ nor f_{MW} . f_{MW} is obtained by extrapolation from the low-frequency flank. That fact that the results agree with Eqs. (6)-(7) down to 1%, supports the procedure. But, to get rid of any doubts high-frequency solution needs to be employed.

5. Conclusions

A finite-element analysis of $\text{SiO}_2@\text{C}$ / epoxy nanocomposites has considered seventeen representative volumes and 1337 converged frequency points to determine the influencing factors and the extent of the Maxwell-Wagner-Sillars response.

Filler loading alone sets the magnitude of the interface effect. Permittivity increases from 3.60 to 6.32 between 0 and 20 vol.%, follows the Maxwell-Garnett result for an infinitely conducting filler inclusion to within 0.34%, and remains the same to within 2 ppm for $2.9\times$ and $5\times$ of core diameter and shell thickness respectively. Because of this, a synthesis dispersity does not threaten the value of permittivity, and no geometric fine-tuning could be effective.

The dimensionless core-to-particle volume ratio $\beta = (a/b)^3$ determines the timescale and size is irrelevant: two different cells having the same $\beta = 0.4705$, but with one of them having twice the sizes show the same spectrum within the error of ± 0.01 ppm. Loading just shifts relaxation by -15.8% linearly, without saturation at all.

In all instances of the study, the interfacial (MWS) relaxation happened within 23.1-70.5 GHz, about 700 times higher than the practical measurement range. Because of this, an MWS peak in these composites cannot be considered as weak or absent, they are fully developed and saturated but spectrally hidden. Because permittivity and DC leakage are enhanced by an identical geometric factor, adding filler moves the material along a fixed trade-off rather than improving it.

Fundamentally both issues stem from the same thing that is the conductive shell DC-connected to matrix, and both could be solved by an additional outer insulating shell. The validated model can analytically explain that if one layer of silica about ~ 0.5 -10 nm thick is put between the $\text{SiO}_2@\text{C}$ and matrix then DC conductivity falls to the insulating-inclusion limit, below that of the unfilled matrix and the frequency at which impedance curve bends will drop from 49.9 Hz to between 32 and 37 Hz, a factor that has always remained the

same throughout this simulation and as a result would be a very clean test of that occurrence. The next thing to do, following this prediction, is a finite-element modeling of the $\text{SiO}_2@\text{C}@\text{SiO}_2$ structure.

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References

- [1] R. C. Smith, C. Liang, M. Landry, J. K. Nelson, L. S. Schadler, "The mechanisms leading to the useful electrical properties of polymer nanodielectrics," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 15, no. 1, pp. 187-196, 2008.
- [2] S. Singha, M. J. Thomas, "Dielectric properties of epoxy nanocomposites," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 15, no. 1, pp. 12-23, 2008.
- [3] I. Pleša, P. V. Nottingher, S. Schlögl, C. Sumereder, M. Muhr, "Properties of polymer composites used in high-voltage applications," *Polymers*, vol. 8, no. 5, 173, 2016.
- [4] K. W. Wagner, "Erklärung der dielektrischen Nachwirkungsvorgänge auf Grund Maxwellscher Vorstellungen," *Arch. Elektrotech.*, vol. 2, pp. 371-387, 1914.
- [5] R. W. Sillars, "The properties of a dielectric containing semiconducting particles of various shapes," *J. Inst. Electr. Eng.*, vol. 80, pp. 378-394, 1937.
- [6] T. J. Lewis, "Interfaces are the dominant feature of dielectrics at the nanometric level," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 11, no. 5, pp. 739-753, 2004.
- [7] L. S. Schadler, S. K. Kumar, B. C. Benicewicz, S. L. Lewis, S. H. Harton, "Designed interfaces in polymer nanocomposites: a fundamental viewpoint," *MRS Bull.*, vol. 32, no. 4, pp. 335-340, 2007.
- [8] M. Roy, D. K. Das, B. K. Dey, S. K. Sen, "Influence of filler shape and size on the dielectric behaviour of epoxy resin / BaTiO_3 composites," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 11, no. 5, pp. 739-747, 2004.
- [9] F. Kremer, A. Schönhals (Eds.), *Broadband Dielectric Spectroscopy*, Springer, Berlin, 2003.
- [10] G. Patil, R. A. Gerhardt, "Simulation of dielectric response and electric field distribution in SiO_2 -coated carbon black / epoxy nanocomposites," *ACerS Annual Spring Meeting*, Seattle, WA, 2026.
- [11] COMSOL Multiphysics® v. 6.2, COMSOL AB, Stockholm, Sweden, 2024.
- [12] Gerhardt, R. A. (2020). *Impedance and dielectric spectroscopy of materials and devices*. John Wiley & Sons.
- [13] A. Sihvola, *Electromagnetic Mixing Formulas and Applications*, IEE, London, 1999.
- [14] E. Barsoukov, J. R. Macdonald (Eds.), *Impedance Spectroscopy: Theory, Experiment, and Applications*, 2nd ed., Wiley, Hoboken, 2005.
- [15] R. A. Gerhardt, "Impedance and dielectric spectroscopy revisited: distinguishing localized relaxation from long-range conductivity," *J. Phys. Chem. Solids*, vol. 55, no. 12, pp. 1491-1506, 1994.
- [16] A. K. Jonscher, "The 'universal' dielectric response," *Nature*, vol. 267, pp. 673-679, 1977.