Effective permittivity of composite elastomer with account of electric conductivity of phases and imperfect interface

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Abstract

The homogenization problem of micromechanics in application to the effective permittivity of particulate composite elastomer with conducting constituents and imperfect interface is studied. The available in literature theoretical models are critically reviewed and the typical problems with interpretation of experimental data are addressed. The imperfect dielectric phases is pointed out as a probable reason of the discrepancy between the theory and experiment. It has been shown that taking the electric conductivity of the composite constituents into account greatly improves accuracy of the predictive models. The Maxwell-Wagner model has been extended to composite dielectrics with imperfect interface. Some possible directions of further research are outlined.

Keywords: composite elastomer, permittivity, conductivity, frequency, homogenization, imperfect interface.

1. Introduction.

Dielectric composite elastomers are now widely recognized as a highly promising material for a variety of applications including energy harvesting and robototechnics (e.g., Perline (1998, 2000)). Performance of these materials is affected greatly by their electromechanical coupling which is, in turn, a quadratic function of permittivity (Landau and Lifshitz, 1984). According to Bortot et al (2014), combination of dissimilar materials is an effective way to produce high permittivity soft composites, as demonstrated both experimentally (Gallone et al, 2007; Molberg et al, 2010; Stoyanov et al, 2011; Rissee et al, 2012) and theoretically (Ponte Castañeda and Siboni, 2012; Tian et al, 2012; Gei et al, 2013; Rudykh et al, 2013). Macroscopic, or effective permittivity of composite may be greatly improved by the purposeful tailoring the microstructure of composite. In so doing, it is important to identify the leading factors which affect composite performance and ensure their proper values in the manufacturing process. This requires a clear understanding the "structure - properties" relationships which can be established by the means of micromechanics.

Effective permittivity of heterogeneous solids has been paid a considerable attention starting from the works of Mossotti (1850), Clausius (1858) and Maxwell (1873). Since that time, the advanced analytical and numerical homogenization schemes developed for the effective conductivity of composite (see, e.g. Bőhm (2016) for a review). Noteworthy, the equations describing several transport phenomena (thermal and electrical conductivity, mass diffusivity, dielectric permittivity, magnetic permeability, optical refractivity) are known to be

mathematically equivalent. This means that the results obtained for one transport property are transferrable to other transport properties of composite including the dielectric constant. However, these advanced and scientifically substantiated results do not find, as a rule, application to composite dielectrics.

Moreover, it turns out that the theoretical models expressing the dielectric constant of heterogeneous solids in terms of the dielectric constants of components fail when it comes to prediction of the properties of ferroelectric ceramic/polymer composites. For example, the experimental data on permittivity of composite reported in Furukawa et al (1976), Yamada et al (1982), Ng et al (2000), Gallone et al (2007) and several other publications show quite a large systematic deviation from the Maxwell (1873) theory.

The possible reason for the observed discrepancy is that the above mentioned theoretical models consider the composite constituents as perfect dielectrics whereas many materials (in particular, polymers) along with dielectric properties possess also electrical conductivity. In this case, both the permittivity and conductivity of constituents affect the overall electric behavior of composite. Wagner (1914) was first to extend the Maxwell (1873) formula to composites made of imperfect dielectric constituents under action of harmonic far field. This and subsequent (Sillars, 1937; Fricke, 1953; Van Beek, 1960; among others) publications explain a nature of such features as dielectric loss and frequency dependence of the effective dielectric constant of composite.

Interface is well known as an important factor affecting the composite's behavior in real world. This is fully applicable to composite dielectrics where the interfaces play a particularly important role. Noteworthy, a vast majority of the theoretical models of composites involve the "perfect interface" assumption which is rather exception than a rule. The real interface may be imperfect due to several reasons including the atomic lattices mismatch, poor mechanical or chemical adherence, surface contamination, oxide and interphase diffusion/reaction layers, debonding, etc. These phenomena affect the bulk properties of composite and make them size-dependent. One can expect that the total interface contribution can become very significant as the particle diameter is reduced. According to Lewis (2004), interfaces are the dominant feature of dielectrics at the nanometer level so the nanocomposites are expected to possess exceptional dielectric properties (Lopez-Pamies et al, 2014).

In this paper, the macroscopic, or effective permittivity of composite elastomer with imperfect dielectric phases and imperfect interface is addressed. The paper is organized as follows. First, we consider/compare the available in literature experimental data on effective permittivity of composite elastomers and observe their systematic deviation from the well-established theoretical models. Second, we discuss briefly the homogenization problem of micromechanics in application to composites with dielectric constituents and show that the abovementioned discrepancy between theory and experiment is readily eliminated by assuming electro conducting properties of constituents which is supported by the experimental data (e.g., Furukawa et al, 1979). Next, the Maxwell-Wagner model is extended to composites with imperfect (both low- and highly conducing) interface. Parametric study of this basic model has been performed and the possible ways of its refinement/generalization are outlined.

2. Effective permittivity: experimental data and interpretation

In this Section, we analyze the experimental data on effective permittivity ε^* of composite elastomers reported by several authors. To ensure comparability, the data obtained for

similar materials and test conditions were selected for this study. Specifically, a the polymer matrix (0-3 connectivity type) composites are considered. Ferroelectric ceramic powder is used as a reinforcing phase so we have a high phase contrast $\varepsilon_2/\varepsilon_1$. Here and below, ε_1 and ε_2 denote permittivity of matrix and particle materials, respectively. The powder particles of approximately the same size and a near-to-spherical shape are randomly and evenly distributed in the matrix, which provides macroscopic isotropy of composite. All the considered works include production of composite samples, measurement their permittivity in low frequency ($10 \div 10^3$ Hz) range by means of broadband dielectric spectroscopy and fitting the obtained data by that or another theoretical model.

We start with the paper by Furukawa et al (1976) who studied the composite of epoxy resin and lead zirconate titanate (PZT) ceramic powder of 0.2 to 2 μm in diameter. Phase contrast $\varepsilon_2/\varepsilon_1 = 1180/4 \approx 300$, measurement frequency 10 Hz. They found that "...magnitude of ε^* was 2 times... greater than the theoretical prediction by Maxwell (1873) theory. The fact that the observed constants were greater than the predictions suggests that PZT ceramics have distorted shape or forming one-dimensional aggregations". However, no evidences in support of this hypothesis were provided.

A binary system consisting of polyvinylidene fluoride (PVDF) and PZT fine powder was studied by Yamada et al (1982). Phase contrast of composite $\varepsilon_2/\varepsilon_1 = 1850/8.9 \approx 200$, measurement frequency 35 Hz. To fit the experimental data, Yamada et al (1982) have suggested the Maxwell type formula for effective dielectric constant of composite with ellipsoidal inclusions and found that the best fit is provided by the model with the ellipsoid axes ratio 2.8 (the shape parameter of model $n = 8.5$) and the long ellipsoids of PZT powder oriented in the applied electric field direction.

The experimental data by Hopkins et al (1992) on permittivity of composite with phase contrast of $\varepsilon_2/\varepsilon_1 = 225/3 = 75$ are taken from the paper by Jayasundere & Smith (1993) who modified the Kerner (in fact, Maxwell) formula for effective permittivity by including (as they believed) pair wise interactions between the neighboring spheres into account. The formula they proposed appears to fit the Yamada et al (1982) experimental data as well.

Ng et al (2000) studied the composites of PZT powder with particle size of 1–3 μm dispersed in a vinylidene fluoride-trifluoroethylene copolymer [P(VDF-TrFE)] matrix prepared by compression molding. Phase contrast $\varepsilon_2/\varepsilon_1 = 120$. Permittivity of the 0-3 composites were measured at 1kHz using a HP4194A impedance/gainphase analyzer. As they noted, the effective permittivity of these composites can be understood in terms of the Bruggeman equation.

Popielarz et al (2001) used the photopolymerization technique for making the model ferroelectric ceramic/polymer composites. Dielectric properties of BaTiO3/PEGDA (poly-ethylene glycol diacrylate) polymer composite with phase contrast $\varepsilon_2/\varepsilon_1 \approx 130$ were measured also using HP4194A analyzer. The obtained data are found to be consistent with the log-law relationship (logarithmic mixing rule) by Lichtenecker (1924) over a broad frequency range.

Gallone et al (2007) studied the dielectric properties of the composite elastomer consisting of PMN–PT (85% of lead magnesium niobate Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and 15% of lead titanate PbTiO$_3$) ferroelectric powder ($\varepsilon_1 = 18600$) dispersed in the polydimethylsiloxane (PDMS) silicone rubber matrix ($\varepsilon_1 = 7.32$). Wideband dielectric spectroscopy was carried out in the frequency range 10 Hz ÷ 100 MHz by means of a vector network analyzer. Also, they tested a number of theoretical models and decided that Bruggeman (1935) formula gave the best match. In fact, this assertion is correct for the frequency 10^3 Hz only.

Kulek et al (2007) studied the BaTiO$_3$/ PVDF nanocomposites of (0–3) type connectivity prepared by hot-pressing. The reported phase contrast $\varepsilon_2/\varepsilon_1 = 1330/8 \approx 166$. Dielectric response of the composites was measured in the frequency range 100 Hz ÷ 1 MHz with computer controlled HP-4284A impedance analyzer. The theoretical models by Lichtenecker (1924) and Yamada et al (1982) were tested and it was found that the Yamada's model with the shape parameter $n = 7$ better fits the experimental data.

The same type (BaTiO$_3$/ PVDF) nanocomposites were fabricated by Li et al (2011) using a simple solution casting process followed by compression molding. The reported there phase contrast $\varepsilon_2/\varepsilon_1 = 500/9.5 \approx 166$. The frequency dependent electrical properties were measured with HP4194A impedance analyzer. The logarithmic mixing rule and Maxwell–Garnett approximation (in fact, Maxwell formula) were used to interpret the experimental data. It was found that they obey the logarithmic mixing rule at high filler content while follow the Maxwell–Garnett approximation at low filler content.

James et al (2013) prepared the PZT/epoxy composites by dielectrophoresis. A donor-doped soft PZT ceramic powder and epoxy resin has a dielectric constant $\varepsilon_2 = 4400$ and $\varepsilon_2 = 4.7$, respectively. The dielectric constant of the composites were measured using Agilent 4263B LCR meter at 1 V and 1 kHz. The experimental dielectric constants of the 0-3 composites match very well with the values predicted by Yamada's model for a shape parameter $n = 4.56$.

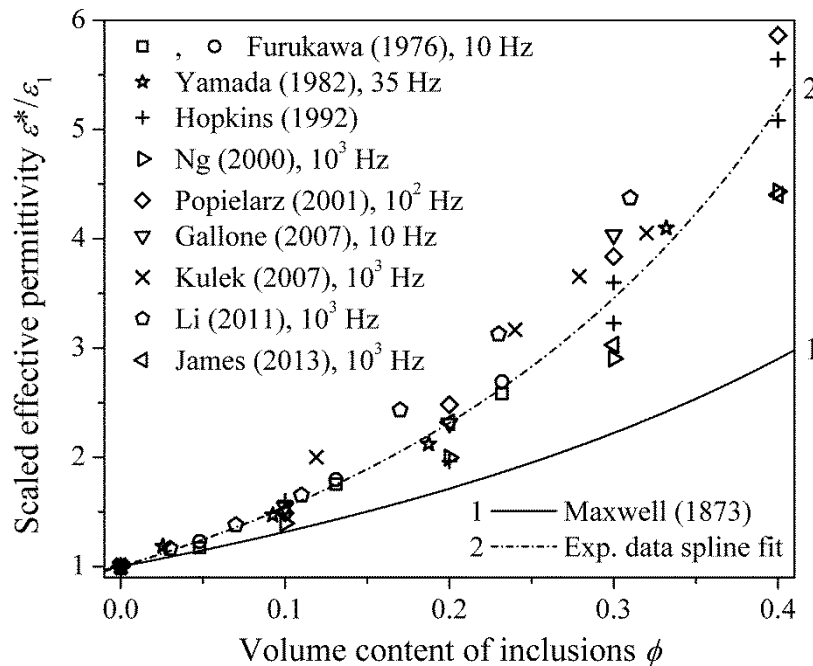This list can be continued although the general trend is already quite obvious, see Fig. 1

Fig. 1. Scaled effective permittivity of composite elastomer with
high phase contrast: experiment vs. Maxwell theory

where the abovementioned experimental values of $\varepsilon^*/\varepsilon_1$ are shown as a function of volume content of disperse phase/filler. The low frequency data by Furukawa et al (1976), Yamada et al (1982), Hopkins et al (1992), Ng et al (2000), Gallone et al (2007), Kulek et al (2007), Li et al (2011) and James et al (2013) are depicted by the discrete symbols. The numerical values are obtained by digitizing the scans of the paper hardcopies so their accuracy is limited by the printing quality and resolution of scans. The solid curve 1 represents the Maxwell (1873)

theoretical prediction. The dash-dotted curve 2 is a spline approximation of these data added just to improve readability of the plot.

As seen from the plot, the experimental points show quite similar behavior which is expected because in all the works we mentioned the random structure composite dielectric with polymer matrix and near-to-spherical ferroelectric powder (high phase contrast $\varepsilon_2/\varepsilon_1$) low frequency measurements. The scatter of the experimental data is quite expected because the results we compare were obtained for materials of various composition, component properties, particle size, manufacturing technology, etc., and measurements were made on different equipment and different frequencies. These and other mentioned in the text but not shown in the figure data reveal a general trend, namely, quite a large systematic discrepancy between the Maxwell (1873) theory and experiment. This is a *very unexpected and strange* fact because Maxwell (known also as Clausius-Mosotti, Maxwell-Garnett, Kerner, etc.) formula is commonly recognized as one of the most reliable homogenization schemes of micromechanics working well at least for the moderate volume content of filler.

The various explanations of this fact have been suggested by the authors but, unfortunately, *none* of them can be regarded as convincing/satisfactory. It is noteworthy that in all the reviewed above paper (with the exception of Furukawa et al (1976)), the formulas used to interpret the results provide (in the authors' opinion) better approximation to the experimental data than Maxwell formula does. The question arises: *can the observed discrepancy between theory and experiment be due to the fact that Maxwell's formula is less accurate than other formulas*? Or, maybe, some another reason (e.g., ignoring the essential physical factors) exists? To answer this question, we turn to micromechanics and carry out one more comparative analysis, this time of the abovementioned theoretical models and formulas for predicting the effective dielectric properties of composite.

3. Effective permittivity: theory

3.1. Homogenization problem

The homogenization problem of micromechanics consists in finding the macroscopic, or effective, properties of heterogeneous solids in terms of the properties of constituents and microstructure parameters. Here, we consider a binary composite consisting of the continuous matrix and discrete particles. Also, we assume the particles to be spherical and equally sized; their perfectly random distribution in the matrix plus isotropy of the constituents results in the macroscopic isotropy of composite.

In the context of electrostatics, the standard homogenization problem consists in finding the effective dielectric constant ε* defined by the relation $\langle \mathbf{D} \rangle = \varepsilon * \langle \mathbf{E} \rangle$ between the macroscopic electrical displacement **D** and electric field **E**. The angle brackets denote averaging over the representative volume element (RVE) of composite. The governing equations for the local (in-phase) fields are given by the formulas

$$\nabla \cdot \mathbf{D}_i = 0; \quad \mathbf{D}_i = \varepsilon_i \mathbf{E}_i = \varepsilon_i \nabla \varphi_i \qquad (1)$$

where φ is the potential; $i = 1$ for matrix and $i = 2$ for inclusions. In the case of constant ε_i, the problem is linear and the equations (1) result in $\nabla^2 \varphi = 0$. For the time being, we assume perfect

interface bonding of composite constituents, i.e., continuity of potential φ and normal electrical displacement $D_n = \mathbf{D} \cdot \mathbf{n} = \varepsilon \, \partial \varphi / \partial n$:

$$[[\varphi]]_S = 0; \quad [[D_n]]_S = 0; \tag{2}$$

where $[[f]]_S$ means a jump of the quantity f across the interface S.

3.2. On accuracy of the single particle models of composite dielectric

We mentioned already a number of formulas for the effective permittivity of composite known in literature. From publication to publication, that or another formula is claimed as most accurate because it provides the best agreement with a specific set of experimental data. However, the real accuracy of these formulas never been addressed. Here, we perform an asymptotic analysis of the some widely used theoretical models. They are listed below.

Maxwell (1873) formula (often referred in dielectric context as Clausius-Mossotti, Maxwell-Garnett, Kerner, etc.) in terms of dielectric constants takes the form

$$\varepsilon^* = \varepsilon_1 \frac{2\varepsilon_1 + \varepsilon_2 + 2\phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2 - \phi(\varepsilon_2 - \varepsilon_1)}. \tag{3}$$

The linearized version of (4) is known as the Landau-Sillars or "dilute limit" formula (Sillars, 1937; Landau and Lifshitz, 1984)

$$\varepsilon^* = \varepsilon_1 \left(1 + 2\phi \frac{\varepsilon_2 - \varepsilon_1}{2\varepsilon_1 + \varepsilon_2} \right). \tag{4}$$

Lichtenecker (1924) log-law relationship (logarithmic mixing rule) is

$$\log\left(\frac{\varepsilon^*}{\varepsilon_1} \right) = \phi \log\left(\frac{\varepsilon_2}{\varepsilon_1} \right). \tag{5}$$

Bruggeman (1935) formula

$$\frac{\varepsilon_2 - \varepsilon^*}{\varepsilon_2 - \varepsilon_1} = \left(\frac{\varepsilon^*}{\varepsilon_1} \right)^{1/3} (1 - \phi) \tag{6}$$

is known also as effective medium approximation.

Yamada et al (1982) formula

$$\varepsilon^* = \varepsilon_1 \frac{(n-1)\varepsilon_1 + \varepsilon_2 + (n-1)\phi(\varepsilon_2 - \varepsilon_1)}{(n-1)\varepsilon_1 + \varepsilon_2 - \phi(\varepsilon_2 - \varepsilon_1)} \tag{7}$$

where n is the parameter attributed to the shape of the ellipsoidal particles represents an extension of Maxwell formula (4) to the matrix type composite with equally oriented ellipsoidal inclusions. In fact, this is exactly the formula derived 60 years earlier by Fricke (1924).

Jayasundere & Smith (1993) suggested another generalization of Maxwell formula in the form

$$\frac{\varepsilon_c}{\varepsilon_1} = \frac{1 - \phi + 3\varepsilon_2 \phi/(\varepsilon_2 + 2\varepsilon_1)[1 + 3\phi(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)]}{1 - \phi + 3\phi\varepsilon_1/(\varepsilon_2 + 2\varepsilon_1)[1 + 3\phi(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)]} \tag{8}$$

by taking into account the pair wise interactions between the neighboring spheres. It should be noted, however, that their analysis is incomplete. In order to take the pair wise interactions into account properly, the solution of two-particle problem must be averaged over all the possible relative positions of spheres using two-point correlation function of the random spatial distribution of particles. For the correct analysis, see Jeffrey (1973).

To simplify our analysis, we put $\varepsilon_2/\varepsilon_1 = \infty$ (which is close to the high phase contrast composite we consider). First, it is readily seen that the logarithmic mixing rule (5) fails in this case. It predicts infinitely large effective permittivity of matrix type composite even for a very small volume content of perfectly conducting inclusions. This clearly absurd result proves that the logarithmic mixing rule *does not apply* to composites with 0-3 connectivity type structure. Due to this reason, the formula (5) is excluded from the further considerations.

For the rest of the models, we find their asymptotic (virial) expansion in the form

$$\frac{\varepsilon^*}{\varepsilon_1} = 1 + A_1\phi + A_2\phi^2 + A_3\phi^3 ...$$

(9)

The resulting formulas are as follows.

Landau-Sillars: $$\frac{\varepsilon^*}{\varepsilon_1} = 1 + 3\phi$$ (10)

Maxwell: $$\frac{\varepsilon^*}{\varepsilon_1} = \frac{1+2\phi}{1-\phi} = 1 + 3\phi + 3\phi^2 + O(\phi^3)$$ (11)

Bruggeman: $$\frac{\varepsilon^*}{\varepsilon_1} = \frac{1}{(1-\phi)^3} = 1 + 3\phi + 6\phi^2 + O(\phi^3)$$ (12)

Yamada: $$\frac{\varepsilon^*}{\varepsilon_1} = \frac{1+(n-1)\phi}{1-\phi} = 1 + n\phi + n\phi^2 + O(\phi^3)$$ (13)

Jayasundere & Smith: $$\frac{\varepsilon^*}{\varepsilon_1} = \frac{1+2\phi+9\phi^2}{1-\phi} = 1 + 3\phi + 12\phi^2 + O(\phi^3)$$ (14)

Jeffrey: $$\frac{\varepsilon^*}{\varepsilon_1} = 1 + 3\phi + 4.51\phi^2 + O(\phi^3)$$ (15)

First, we observe that the linear terms in all the expansions but (13) are identical. This result is expected because $O(c)$ is the only structure-independent term in (9) and so can be determined from the single particle based model of macroscopically isotropic composite. The formula (13) falls in this row only for $n = 3$ corresponding to spherical particle shape. On the contrary, $O(c^2)$ and higher order terms are structure-dependent as in principle cannot be found in the framework of single-inclusion approximation. This means that all the single inclusion-based models that neglect the effect of microstructure and interaction between the inclusions are *equivalent* in accuracy. Strictly speaking, their application is justified only to composites with a low volume content of inclusions c. On the contrary, the formula (15) takes the pair wise interactions and radial distribution (two-point correlation function) of particles into account. According to Jeffrey (1973), for the well-stirred distribution of particles the $O(c^2)$ coefficient A_2

equals 4.51 which is much closer to Maxwell formula with $A_2 = 3$ and to Bruggeman (1935) with $A_2 = 3$ than to Jayasundere & Smith (1993) where $A_2 = 12$.

However, the final verdict regarding the predictive ability of that or another approximation can be done only after comparison with the benchmark data. It is seen from Fig. 2 that the predictions of two dissimilar *rigorous* methods, they the Brownian motion simulation (Kim and Torquato, 1991) and the multipole expansion method (Kushch, 2013) where the microstructure of composites and interactions between the particles have been adequately taken into account are very close to each other and so they can be regarded as a benchmark for the available in literature approximate theories. As would be expected, the Maxwell formula (being the lower Hashin-Shtrikman bound for effective property) underestimates the benchmark data but appears to be closest to them. The Landau-Sillars model has to be rejected as violating the lower Hashin-Shtrikman bound whereas two other (Bruggeman (1935) and Jayasundere & Smith (1993)) formulas greatly overestimate the effective permittivity of composite.
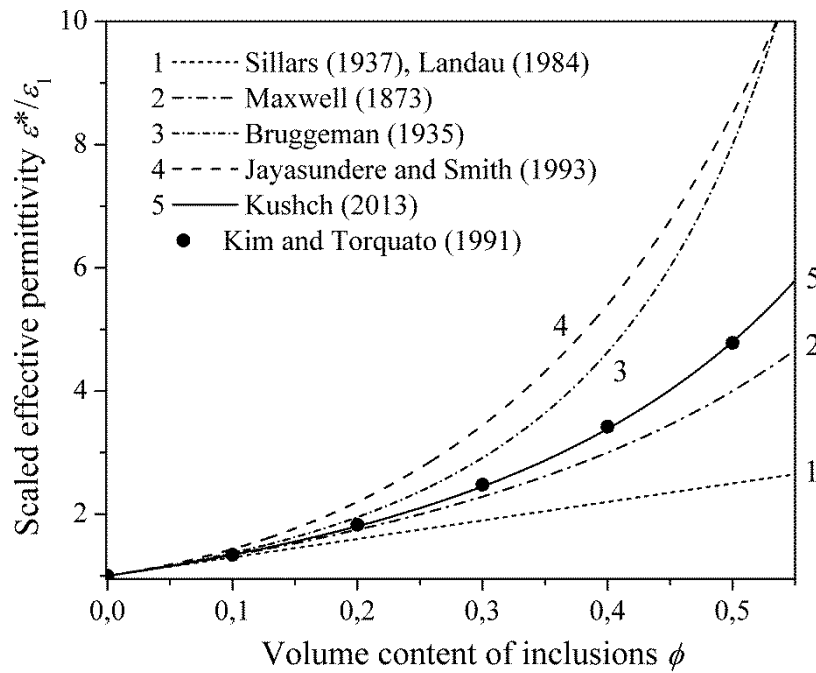

Fig. 2. Scaled effective permittivity of macroscopically isotropic random structure composite with spherical inclusions and high phase contrast (theory)

The formula (7) has been derived, as we mentioned already, by Fricke (1924) for composite with equally oriented ellipsoidal inclusions and predicts, among other things, anisotropy of its dielectric properties. Its application to the isotropic composite with spherical inclusions in a way (Yamada et al, 1982; Kulek et al, 2007; James et al, 2013; among others) where the shape parameter n not relate the actual shape of inclusions but treated as a fitting parameter, is incorrect and reduces this formula to the category of fitting curves and spline approximations.

In this regard, it seems appropriate to recall the *fundamental difference* between the fitting curves (to whom, in particular, the logarithmic mixing rule (5) belongs) and the micromechanical models of composite derived from the structure model and physical laws/equations. The latter represents a scientific result and enables an adequate prediction of the

behavior of composite provided the adopted structure and physical model are close to the material under consideration.

4. Composite dielectric with conducting phases

The above comparison confirms reliability of Maxwell model but provides no explanation to the observed in Fig. 1 discrepancy between the theory and experiment. The experimental data by Gallone et al (2007) provide a useful hint for understanding the root of the problem. Indeed, they show quite clearly that the effective permittivity of dielectric composite is a *frequency-dependent* property.
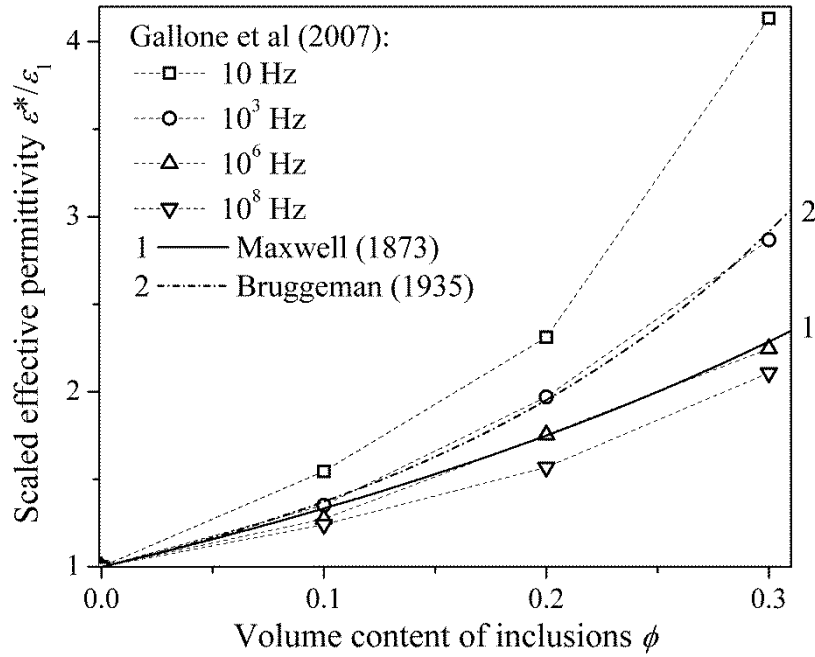

Fig. 3. Scaled effective permittivity of the silicone/PMN–PT composite
as a function of filler volume content

In Fig. 3, the data by Gallone et al (2007) are plotted vs. volume content of inclusions. As seen from the plot, the effective permittivity measured at 10 Hz greatly exceeds all the theoretical predictions. For 10^3 Hz, their data indeed are fitted well by the Bruggeman formula. At the same time, the best fit for 10^6 Hz is provided by the Maxwell's theory. For 10^8 Hz, the dielectric constant of composite falls below the level predicted by Maxwell formula being the lower Hashin-Shtrikman bound for effective conductivity. This indicates that for 10^8 Hz and above the volumetric properties of constituents are also affected by frequency of the electric field.

In fact, this phenomenon is known for a quite long time. It was Wagner (1914) who has extended Maxwell model to composites whose constituents possess both dielectric permittivity ε_i and electrical conductivity σ_i. Provided the applied electric field is a harmonic function of time with frequency ω [1/s]:

$$\mathbf{E} = \mathbf{E}_a \exp(i\omega t),$$
(16)

the governing equations for the total current are as follows:

$$\nabla \cdot \mathbf{j} = 0; \quad \mathbf{j} = \sigma\mathbf{E} + \frac{\partial \mathbf{D}}{\partial t} = (\sigma + i\omega\varepsilon)\mathbf{E}. \tag{17}$$

By analogy with (2), the perfect bonding conditions at the spherical matrix-inclusion interface are written as

$$[\![\varphi]\!]_S = [\![\mathbf{j} \cdot \mathbf{n}]\!]_S = 0. \tag{18}$$

It is readily seen form the analogy considerations that solution to the homogenization problem for composite with conducting constituents can be obtained by formal replacing the permittivity ε_i in the formula (3) with its complex counterpart, $e_i = \varepsilon_i - i\sigma_i/\omega$:

$$\varepsilon^* = \varepsilon'^* - i\varepsilon''^* = e_1 \frac{e_2 + 2e_1 + 2\phi(e_2 - e_1)}{e_2 + 2e_1 - \phi(e_2 - e_1)}. \tag{19}$$

The Maxwell-Wagner formula predicts the Debye type frequency effect of composite permittivity:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau_r}, \quad \tau_r = \frac{\varepsilon_2 + 2\varepsilon_1}{\sigma_2 + 2\sigma_1}, \tag{20}$$

τ_r being the characteristic relaxation time. It follows from (20) that electrical (even very low) conductivity of composite constituents makes its effective properties dependent on the frequency of applied electric field. As a consequence, the formulas derived in assumption of perfect dielectric phases are not applicable to these materials.

In Fig. 4, the low-frequency (~10 Hz) experimental data are reproduced from Fig. 1, the high-frequency (10^6 Hz) data by Gallone et al (2007) are shown by the solid triangles. The dash-dotted curves 1 and 2 are calculated using the formula (19) for $\omega = 10$ and $\omega = 10^6$, respectively.
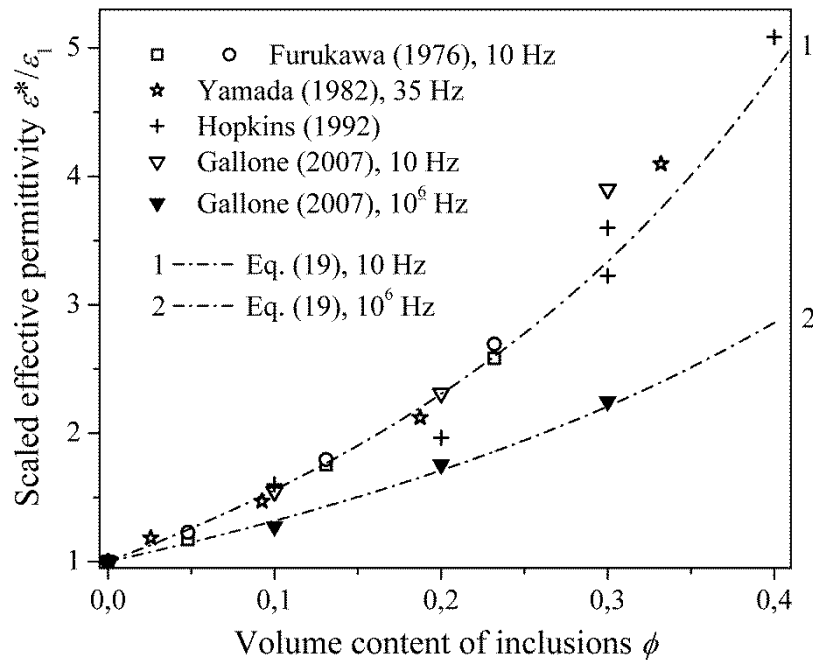

Fig. 4. Scaled effective permittivity of the composite elastomer with conducting matrix as a function of filler volume content and frequency of the applied electric field

The values of permittivity and electrical conductivity of polymer matrix ($\varepsilon_1 = 2.5 \times 10^{-10}$ F/m, $\sigma_1 = 6.4 \times 10^{-8}\ (\Omega \cdot m)^{-1}$) and piezo ceramic inclusion ($\varepsilon_2 = 1.7 \times 10^{-8}$ F/m, $\sigma_2 = 0$) is taken from Furukawa et al (1979). As seen from the plot, Maxwell-Wagner model provides a reasonable accuracy of theoretical prediction for the high frequency (where an effect of conductivity is small and so (19) reduces to Maxwell formula) as well as for - what is important - low frequency regime where the composite dielectric elastomers are supposed to work.

We must admit that the above comparison is not entirely correct. Indeed, the values of the electrical conductivity of phase materials in most works were not provided so they have been taken for calculations from a single source (Furukawa et al, 1979). Nevertheless, the data in Fig. 4 show quite convincingly the need to take the electrical conductivity of phases into account for predicting the effective permittivity of composite elastomers.

Summing up our analysis, we note the following. The frequency dependence of the effective permittivity of composite elastomers reported in the above cited experimental works unambiguously indicates the presence of phase conductivity. At the same time, the models used there take the phase materials as perfect dielectrics. This contradiction is the real cause of the discrepancy between these models and experiment.

5. Composite dielectric with imperfect interface

The models we have considered so far are also based on the "perfect interface" assumption which is rather exception than a rule in real world. There are several reasons for real interface to be imperfect including atomic lattices mismatch, phonons scattering, poor mechanical or chemical adherence, surface contamination, oxide and interphase diffusion/reaction layers, debonding, etc. These phenomena affect the bulk properties of composite and make them size-dependent, at least on a certain length scale. One can expect that the total interface contribution can become very significant as the particle diameter is reduced. According to Lewis (2004), interfaces are the dominant feature of dielectrics at the nanometer level so the nanocomposites are expected to possess exceptional dielectric properties (Lopez-Pamies et al, 2014).

There is a rather limited body of papers devoted to modeling the interface phenomena in composite dielectrics. In these works, an interface is modeled by the interphase layer whose thickness and properties must be taken from some other considerations (Vo and Shi, 2002; Murugaraj et al, 2005; Todd and Shi, 2005; Lopez-Pamies et al, 2014). An alternate approach consists in modeling an imperfect interface of composite by the properly modified interface conditions. This approach is quite efficient and well known in micromechanics (see Hasselman and Johnson, 1987; Lipton, 1998; Miloh and Benveniste, 1999; among others) but, to the best knowledge of the authors, never been applied to the composite dielectrics.

Here, we consider two "imperfect" counterparts of the matrix-inclusion interface (18), they are so-called low conducting (LC) interface:

$$[\![\mathbf{j} \cdot \mathbf{n}]\!]_S = 0; \quad h_c [\![\varphi]\!]_S = -(\mathbf{j} \cdot \mathbf{n})_S; \tag{21}$$

and highly conducting (HC) interface:

$$[\![\varphi]\!]_S = 0; \quad [\![\mathbf{j} \cdot \mathbf{n}]\!]_S = \nabla_s \cdot \mathbf{j}_s = h_s \nabla_s^2 \varphi. \tag{22}$$

where ∇_s^2 denotes surface Laplacian. These conditions involve the constants (h_c in (21) and h_s in (22)) being the material (dimensional) parameters of interface and in the limiting cases $h_c = \infty$ and $h_s = 0$ reduce to (18). As to the physical meaning of these conditions, the resistivity type condition (21) introduces discontinuity of potential proportional to the normal current. On the contrary, (22) describes a jump in the normal component of the current produced by the interfacial surface charge density and coupled to the electric potential through a Poisson equation on the interface (Lipton, 1998).

Modification of Maxwell-Wagner formula due to (21) and (22) is straightforward and yields the formula for the complex permittivity of composite with conducting phases and imperfect interface

$$\frac{\varepsilon^*}{\varepsilon_1} = \frac{1 + 2\phi(Y-1)/(Y+2)}{1 - \phi(Y-1)/(Y+2)}, \tag{23}$$

where

$$Y = \frac{e_2}{e_1}\left[1 - 1/\left(\frac{h_c R}{e_2} + 1\right)\right] \tag{24}$$

for LC interface and

$$Y = \frac{e_2}{e_1}\left(1 + 2\frac{h_s}{e_2 R}\right) \tag{25}$$

for HC interface, R being the particle radius. The following advantageous features of this solution are worth to be mentioned.

1. By contrast to the interphase model, we have here a single interface-related parameter which can be uniquely determined from the experiment.

2. The model involves the characteristic length parameter R which results in size effect of effective permittivity. One can expect the interface contribution be very significant with the particle diameter going to nano scale.

3. The model behavior is governed by the dimensionless parameter, or criterion $P = h_c R / e_2$ for LC and $P = h_s/(e_p R)$ for HC. As seen from the formulas (23) to (25), the interface effect is negligible when the criterion P is small but becomes significant when this parameter is $O(1)$.

Some idea of the interface effect can be drawn from the Figs 5 and 6 where the effective permittivity of composite with imperfect interface is shown as a function of the frequency of applied electric field. The phase properties taken for numerical study are the same as in Fig. 4, volume content of ceramic powder $\phi = 0.3$. As seen from these plots, an effect of interface can be quite sound and, in the considered case, manifests itself in the substantial growth of low-frequency permittivity. Noteworthy, these plots are rather illustrative: before applying the developed theory, one has to make sure that (a) the model of interface corresponds to actual composite and (b) the interface parameter is properly measured or estimated from some theoretical considerations.
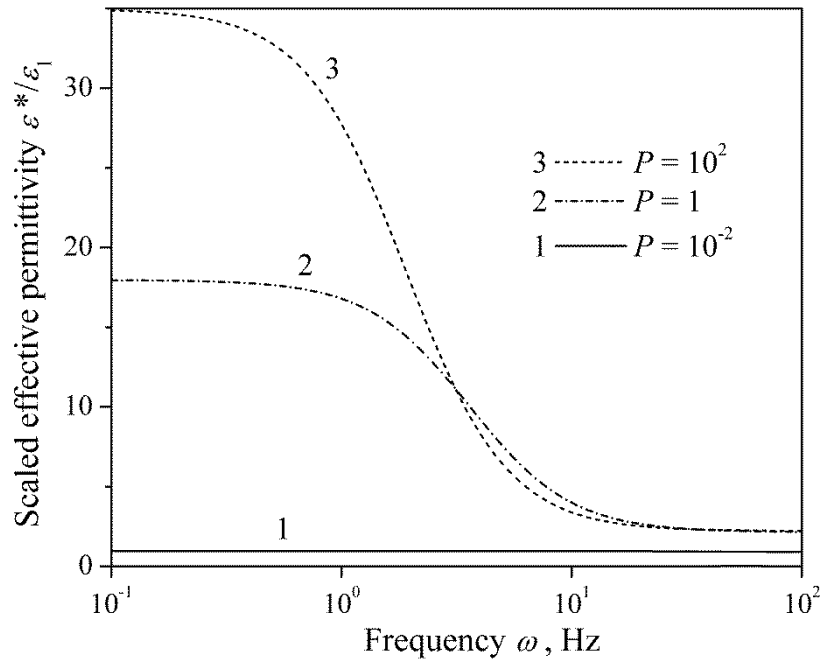
Fig. 5. Scaled effective permittivity of the composite elastomer with conducting matrix and LC interface as a function of the applied electric field frequency
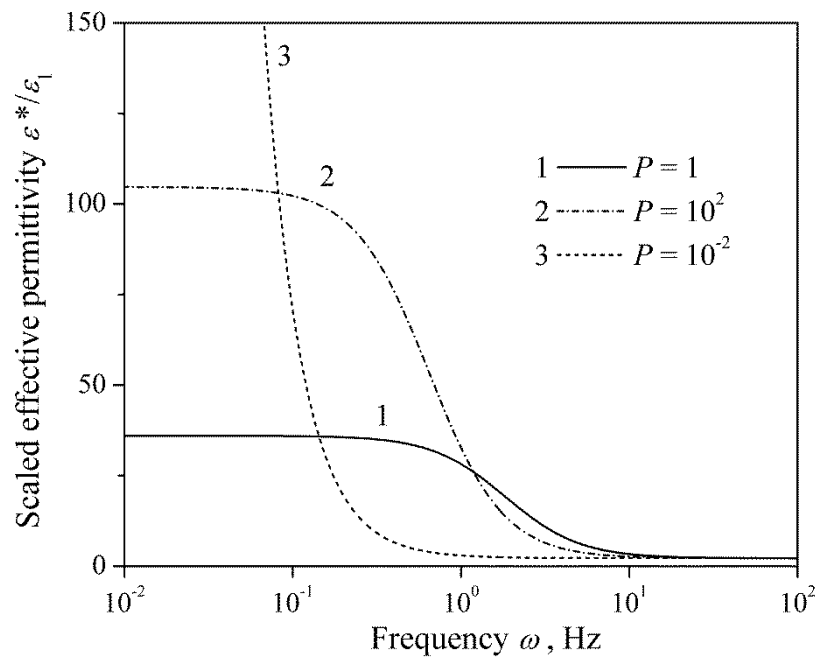

Fig. 6. Scaled effective permittivity of the composite elastomer with conducting matrix and HC interface as a function of the applied electric field frequency

6. Discussion and outlook of the future research

Predicting the macroscopic behavior of composite dielectrics is a non-trivial problem. On the first sight, permittivity looks quite similar to other transport properties, namely, thermal or electrical conductivity, mass diffusion, etc. However, an attempt to interpret the experimental data by means of the standard homogenization schemes of micromechanics fails in most cases. The observed (sometimes quite significant) discrepancy between the theory and experiment is usually attributed to the structural factors (geometry of particles, their arrangement, interaction, etc.) not taken into account in that or another predictive model. At the same time, such physical factors as the phase electrical conductivity and imperfectness of interfaces which significantly affect the behavior of the composite often remain out of sight. This leads to a paradoxical situation when the best agreement with experiment, purely by chance, provide the models that are far from the best (and sometimes simply not enduring critics) from the micromechanical point of view.

The majority of dielectrics - including the elastomers - possess at least small electrical conductivity that makes the behavior and, hence, theoretical description of composites made from these materials more complicated. In addition to the fact that such composites possess both dielectric and conductive properties, they turn out to be frequency dependent, even where the properties of the constituent materials are frequency-independent. The comparative analysis of the available experimental data done in Section 2 shows their large (up to 2 times) systematic deviation from the Maxwell theory. The Maxwell-Wagner model not only eliminates this discrepancy, but also explains its cause, namely the frequency dependence of the properties of the composite elastomer. It should be noted that this model predicts Debye type relaxation in dielectric composite which agrees with experiment only qualitively. Broadening the relaxation time spectrum is possible due to the properties of constituents, particle size distribution, particle interactions, interface effects etc. In particular, already two-particle model (Jeffrey, 1976) predicts a spectrum of relaxation times rather than one value predicted by the single-inclusion model (Wagner, 1914). However, this problem is still open and far from being solved.

The interface phenomena in composite dielectrics and their effect of the macroscopic behavior is another poorly explored area. The available interphase models are valid only for low content of inclusions, perfect dielectric phases (Vo and Shi, 2002; Murugaraj et al, 2005; Todd and Shi, 2005) and "frozen" distribution of charges (Lopez-Pamies et al, 2014). After all, it is unclear how to find the parameters of interphase layer. By contrast, the imperfect interface model we have suggested is free of these limitations. It is also advantageous in that characterizes an interface by a single parameter which can be uniquely determined from the experiment. The model involves also the characteristic length parameter (particle radius) which results in size effect of effective permittivity. One can expect the interface contribution be very significant as the particle diameter is reduced to nano scale - the fact that favorably agrees with experiment. It should be noted that possible models of imperfect interface are in no way limited to (21) or (22). Their modification or generalization is quite possible based on deeper understanding of the interface phenomena.

Further progress in theoretical description of the composite dielectrics can be achieved by taking the microstructure and interaction effects into account with aid of the multi particle models. For now, an effect of microstructure on the effective properties of composite is still mostly unexplored in the electrostatics context. All the models but Jefferey (1973, 1976) we analyzed in this paper are known to be the first order approximations whose application is justified only for the composites with low volume content of filler. In order to obtain a reliable prediction for high-filled composite, one has to use, by analogy with Kim and Torquato (1991)

or Kushch, (2013), the advanced multi-particle structure model able to take the microstructure (shape, size, orientation and arrangement of filler) and interaction effects into account. One promising option here is to follow the approach developed by Kushch et al (2015) where the complete solutions for effective conductivity of spheroidal particle composite of periodic and random micro structure with imperfect interfaces have been derived. Expansion of this approach to the considered permittivity problem for composite elastomer with imperfect dielectric phases and imperfect interface is rather straightforward. To this end, it suffices, by analogy with Wagner (1914), to substitute in all the formulas the real value conductivity of constituents with its complex permittivity counterpart $e_i = \varepsilon_i - \mathrm{i}\sigma_i / \omega$.

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