Applicability of Different Laws of Mixture for Polystyrene-Alumina Composites as Heterogeneous Dielectrics

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ABSTRACT

Ambient dielectric effects have been studied in alumina-polystyrene compacts as functions of frequency and composition to explore the possibility of their use as electronic materials and to characterize them on the basis of existing theories. The dielectric constant ε' and loss ε'' increase with increasing alumina content at each frequency; both parameters decrease with increasing frequency. The extent of interfacial polarization is substantially augmented as the frequency is reduced. ε' and $(\varepsilon')^{-1}$ are both curvilinear in the volume fraction, but ε' shows a break at 70 wt.% in the gravimetric-blend plot, reflecting a change in the pattern and degree of interactions. The systems also conform to both Lichteneker-Rother's logarithmic equation as well as Clausius-Mossotti's equation valid for overall non-polar dielectrics.

The systems are better described by Maxwell-Wagner's equation compared to Bottcher-Bruggeman's equation reflecting a low degree of polymer-filler interaction. The dielectric behaviour of PS-Al_2O_3 systems can also be explained by the non-Debye relaxation theory universally applicable to all dielectrics.

Keywords: dielectric constant, loss factor, heterogeneous dielectrics, law of mixture.

INTRODUCTION

Graded dielectrics having controlled dielectric properties can be obtained from multiphase dispersion of ceramic oxide powder in polymer matrix /1,2/. This kind of heterogeneous dielectrics has certain distinct advantages. These materials have good electrical and mechanical properties and also very good processability. This type of heterogeneous two-component polymer-ceramic composites can be used as materials for capacitor, insulator, and even gradient dielectrics.

The present paper embodies the results of an investigation on the ambient dielectric constant (ε') and loss factor (ε'') of heat-compacted alumina-polystyrene composites as functions of frequency and composition. Alumina has been referred to in the text here with subscript 1, and polystyrene (PS) with subscript 2. The applicability of different formulae suggested for the calculation of permittivity (ε') of the heterogeneous mixtures has also been tested for the present systems.

EXPERIMENTAL

The pure A.R. grade alumina powder (d=3.01 gm/cc) was calcined by heating for 3 hrs. at 1200°C. The general purpose polystyrene (d=1.04 gm/cc) was

dissolved in a minimum quantity of A.R. grade benzene to a thick consistency. The alumina powder was added to the PS solution. The mixture was then stirred vigorously and simultaneously slowly evaporated to dryness at 90°C. The mass was kept overnight in a vacuum desiccator and then pulverised in a mortar. Various such mixtures having compositions of 40, 50, 60, 70 and 80 wt.% of alumina were prepared. Circular pellets having 2.5 cm dia and 0.15-0.2 cm thickness were prepared out of these mixtures in a die and punch system at 110°C under hydraulic pressure, 115 + 5 kg/cm^2. The ambient ε′ and ε″ were measured on these pellets with a Marconi Q-meter (model TF-329G) between 5 x 10^4 and 10^7 Hz.

RESULTS AND DISCUSSION

The semi-log plots of ambient ε′ and ε″ vs. f (Figs. 1 and 2) reveal almost the same features as those exhibited by PS-rutile composites /1/. For example, (1) there is no saturation limit reached by ε′ up to the lowest experimental frequency (5 x 10^4 Hz); (2) the dispersion region spreads down to somewhere between 5 x 10^5 and 10^6 Hz and attains a constant value beyond this region for all the compositions; (3) an increasing alumina content increases ε′ at all frequencies.

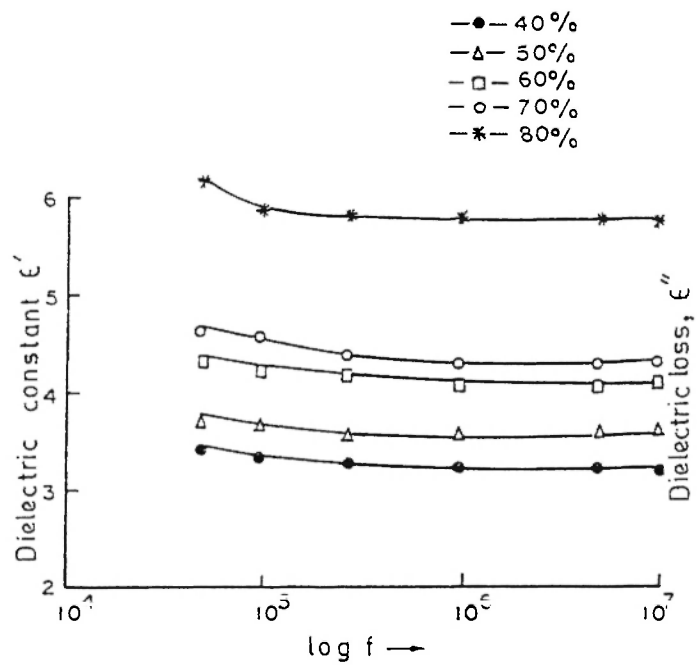

Fig. 1: Semi-log plots of dielectric constant vs. frequency for different wt.% alumina.

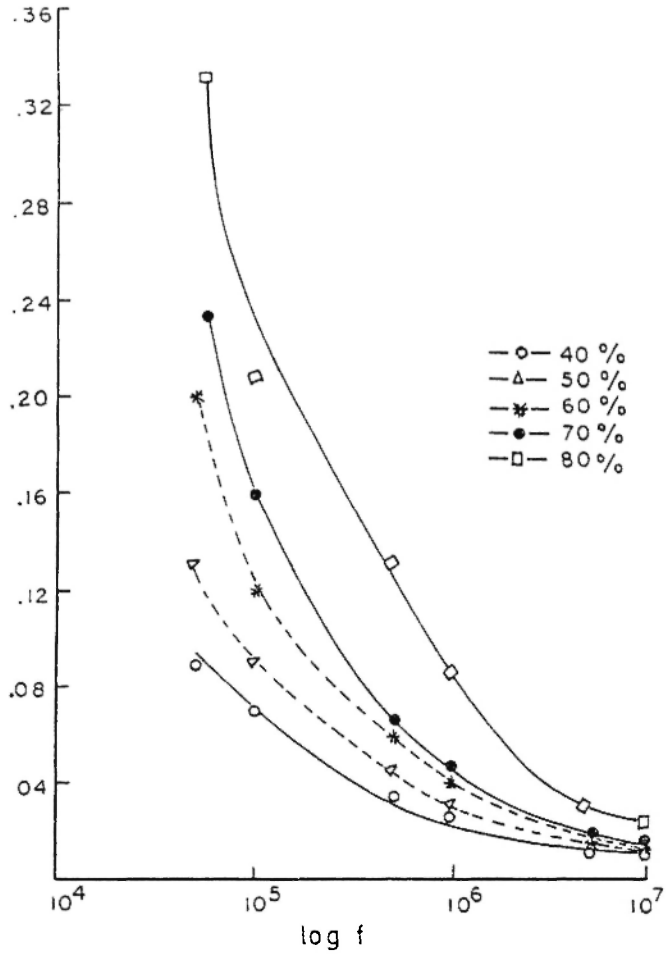

Fig. 2: Semi-log plots of dielectric loss vs. frequency for different wt.% alumina composites.

A similar nature is exhibited in the dependence of dielectric loss ε″ on frequency and composition (Fig. 2). For each frequency, ε″ increases with increase of alumina, and for each composition, ε″ decreases with increase of frequency. This may be interpreted as an augmentation of the extent of space charge polarisation as the frequency is reduced.

It is known that both ε′ and ε″ depend on the electronic, the ionic, the dipole-orientation and the space-charge polarizations; the last effect is more frequently known as the Maxwell-Wagner effect, arising out of some kind of a heterogeneity being present in the sample. It involves masses larger than low-molecular-weight dipoles and exerts its influence

more considerably at lower frequencies. It should, therefore, be appreciably operative at 5 x 10^4 Hz (the lowest frequency in the present series of measurement) and should gradually decay as the frequency is increased. The present system of compact is a multiphase mixture of two dielectrically different materials, where alumina is ionic and polycrystalline and polystyrene is amorphous, atactic and non-polar. Such a mixture with a distinct interphase should be appreciably lossy at low frequencies; and it has displayed a higher space-charge effect owing to Maxwell-Wagner polarization, as expected.

The approximate values of the magnitude of both relative dispersion $(\varepsilon'_L - \varepsilon'_\infty)/\varepsilon'_\infty$ and relative relaxation $(\varepsilon'_L - \varepsilon''_\infty)/\varepsilon''_\infty$, where ε'_L and ε''_L are permittivity and loss factor, respectively, at the experimental lowest frequency f, ε'_∞ and ε''_∞ the ultimate value of ε' and ε'' at the hypothetically infinite (the highest) f. The relative dispersion and relaxation may then be plotted against the composition in wt.% of alumina. It is found from such plots (Fig. 3) that the maxima are attained at 70 wt.% alumina, and this may be related to the maximum of the net dipole moment (charge-displacement) concentration involved in this process /1/.

The log-log plots of σ (AC-conductivity, i.e. the dielectric specific conductivity) against frequency f of the applied electric field (Fig. 4) is found to be linear for all the compositions.

This reflects that the systems conform to Non-Debye Relaxation Theory /3,4/ universally applicable to all dielectrics. According to this theory, loss factor ε'' is a power function of the applied field frequency f, i.e., $\varepsilon'' = Af^{n-1}$, where A and n are two constants and $0<n<1$.

But,

$$\sigma = \frac{\varepsilon'' f}{1.8 \times 10^{12}} = (Af^{n-1} \times f) \times \frac{1}{1.8 \times 10^{12}} = \frac{A}{1.8 \times 10^{12}} f^n$$

Thus log σ vs. log f plots become linear with a slope n, and n varies between 0.445 to 0.60 for the present systems. The lowest value corresponds to 80% and the highest value corresponds to 50% alumina composites.

The polystyrene-alumina mixed systems may be

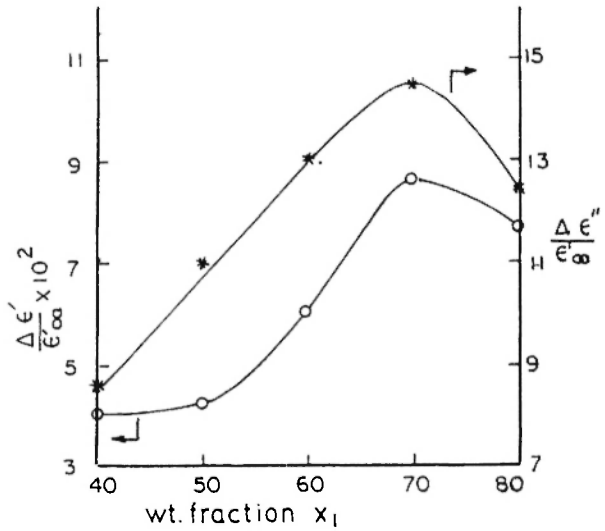

Fig. 3: Plots of relative dispersion $\Delta\varepsilon'/\varepsilon'_\infty$ and relative relaxation of $\Delta\varepsilon''/\varepsilon''$ against weight fraction of alumina.

considered as random dielectrics which are expected to obey Weiner's inequalities given by the equation (1)

$$\sum_{i=1}^{m} v_1/\varepsilon'_i \le \varepsilon' \le \sum_{i=1}^{m} v_i \varepsilon'_i \qquad (1)$$

where v_i is the volume fraction of the i-th component in a statistical mixture of m number of components and ε'_i and ε' are, respectively, the dielectric constant of pure i and the composite. The composite systems are found to obey these Weiner's inequalities at all frequencies.

The majority of formulae used to calculate ε' of heterogeneous random dielectrics based on the law of statistical mixture may be represented in the general form

$$f(\varepsilon') = \sum_{i=1}^{m} v_i f(\varepsilon'_i) \qquad (2)$$

where v_i and ε'_i are the volume fraction and dielectric constant of the i-th component.

For two-component systems, the equation (2) assumes the form

$$f(\varepsilon') = v_1 f(\varepsilon'_1) + (1 - v_1) f(\varepsilon'_2) \qquad (3)$$

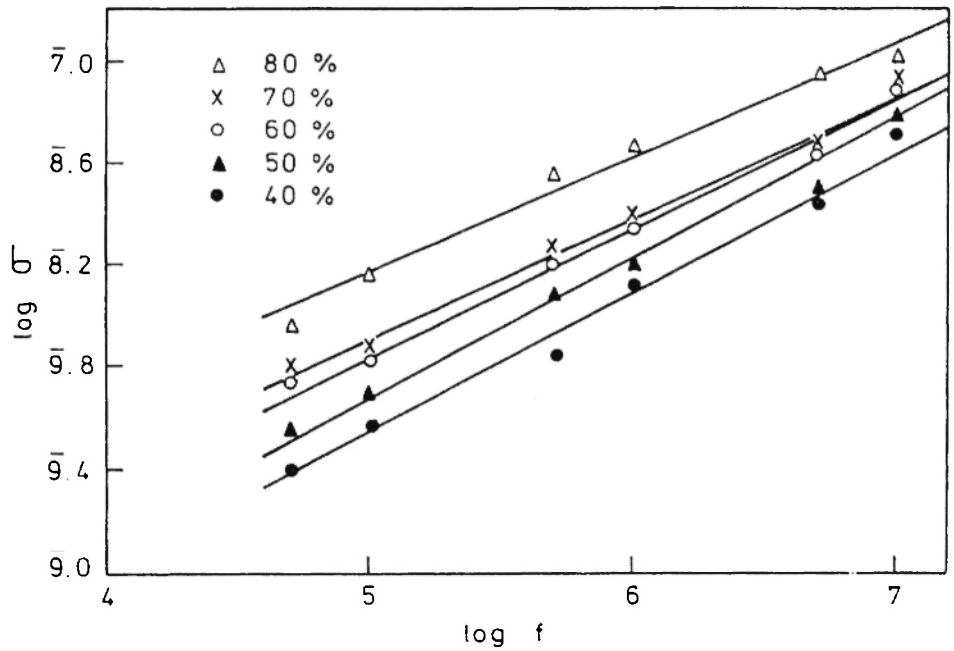

Fig. 4: Log-log plots of ac-conductivity vs. frequency for different wt.% alumina.

where ε'_1 and ε'_2 are the dielectric constants of components 1 and 2, respectively, v_1 is the volume fraction of component 1, f is some function involving the dielectric constant. For the present systems, alumina is considered component 1 and polystyrene component 2.

Figs. 5-7 significantly illustrate the dielectric-interaction pattern of the mixed system with respect to composition. To check the applicability of different equations for the present system, the permittivity values of the compacts and 5 x 10^5 Hz (where dispersion phenomena are still operative) are used.

It is observed that ε' is nonlinearly dependent on the volume fraction v_1 of alumina (Fig. 5) according to the equation

$$\varepsilon' = v_1 \varepsilon'_1 + (1 - v_1) \varepsilon'_2 \qquad (4)$$

This nonlinearity reflects that the valid average is not arithmetic in nature, that is, the constituent dielectrics are not combined in parallel in the composite. The plot of the inverse of the dielectric constant according to the formulae (5) is found to be curvilinear, which indicates that neither are two-component dielectrics in series combination, that is, the

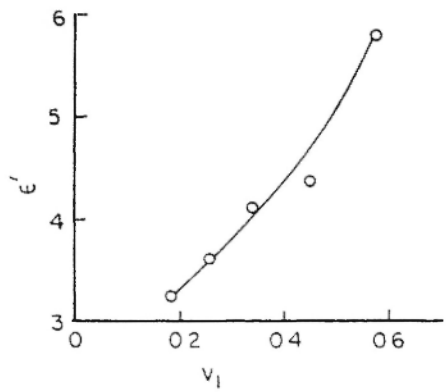

Fig. 5: Plot of dielectric constant ε' vs. V_1 volume fraction of alumina.

valid average is not harmonic in nature (Fig. 6).

$$1/\varepsilon' = \frac{v_1}{\varepsilon'_1} + \frac{1-v}{\varepsilon'_1}\frac{v_1}{\varepsilon'_1} + \frac{1-v_1}{\varepsilon'_2} \qquad (5)$$

However, the systems conform to Lichteneker and Rother's logarithmic equation (6) /5/, appropriate for a layered structure, which are neither parallel nor perpendicular to the applied electric field, where the valid averages are neither arithmetic nor harmonic (Fig. 7).

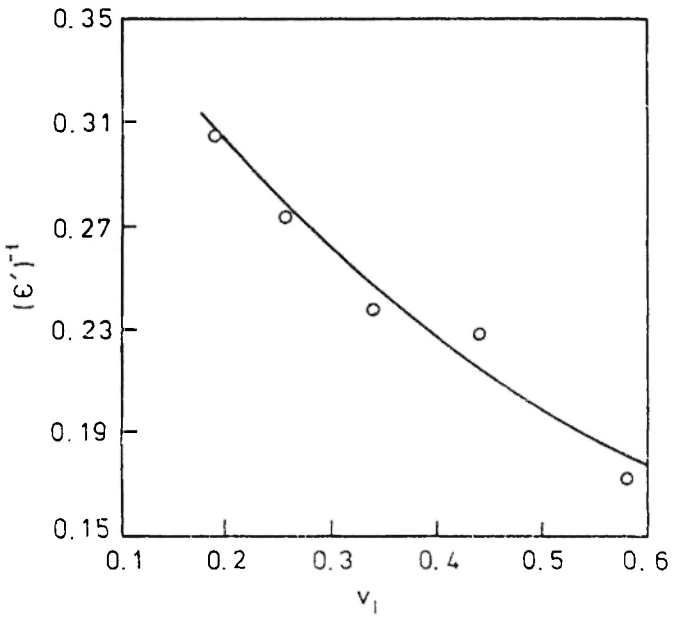

Fig. 6: Plot of inverse of dielectric constant vs. volume fraction of alumina.

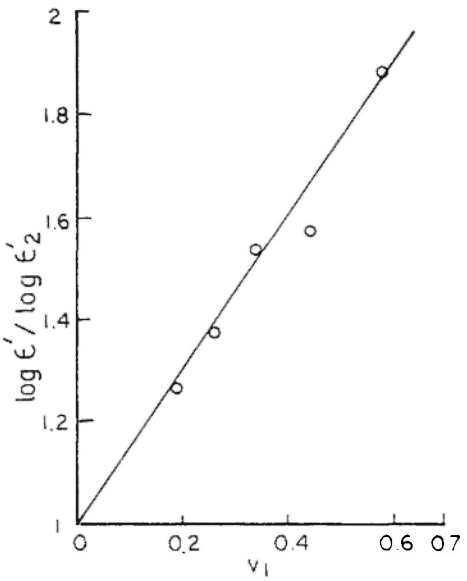

Fig. 7: Plot of Lichteneker-Rother's logarithmic function of dielectric constant against volume fraction of alumina.

$$\log \varepsilon'/\log \varepsilon'_2 = v_1 (\log \varepsilon'_1/\log \varepsilon'_2 - 1) + 1 \qquad (6)$$

where ε'_2 and ε'_1 are the permittivities of pure PS and alumina respectively. The intercept cut off from the ordinate at $v_1 = 0$ when the system is pure PS is exactly unity. However, it is found that ε' is linear in a gravimetric blend composition with a break at 70 wt.% (Fig. 8). This reflects a change in the degree and pattern of interaction as more and more alumina is incorporated and the matrix symmetry changes.

The values of ε' of compacts calculated with the help of Maxwell-Wagner /6,7/ equation (7),

$$\varepsilon' = \varepsilon'_2 \frac{2\varepsilon'_2 + \varepsilon'_1 + 2v_1(\varepsilon'_1 - \varepsilon'_2)}{2\varepsilon'_2 + \varepsilon'_1 - v_1(\varepsilon'_1 - \varepsilon'_2)} \qquad (7)$$

where $\varepsilon'_1 = 9.5$; $\varepsilon'_2 = 2.6$ and the Bottcher-Bruggeman /6/ formula (8),

$$\varepsilon = \frac{1}{4}\left[H + (H^2 + 8\varepsilon'_1\varepsilon'_2)\right] \qquad (8)$$

where $H = (3v_1 - 1)\varepsilon_1 + (2 - 3v_1)\varepsilon_2$, have been plotted against v_1 along with the experimental curve on the same graph (Fig. 9). On careful examination of the three plots, it is found that the experimental ε' is almost identical to the Maxwell-Wagner (MW) ε' up to $V_1 = 0.257$, i.e., $X_1 = 50$ wt.%, beyond which the experimental values are throughout larger. On the contrary, the Bottcher-Bruggeman (BB) values are less than the experimental values in this concentration region. However, at higher alumina content, the experimental plot and BB plot intersect each other at v_1

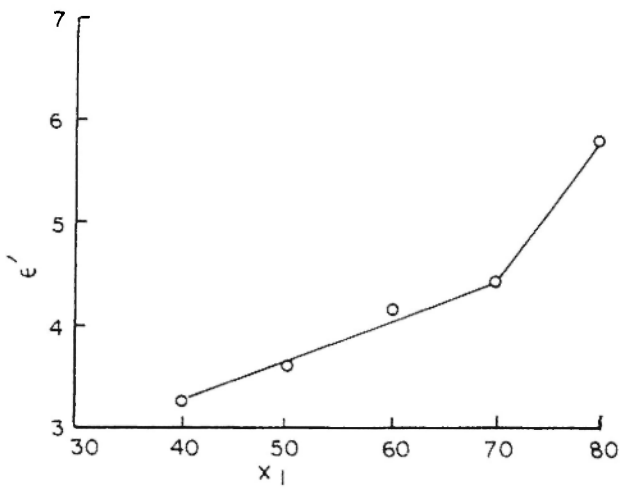

Fig. 8: Plot of dielectric constant ε' vs. X_1 weight fraction of alumina.

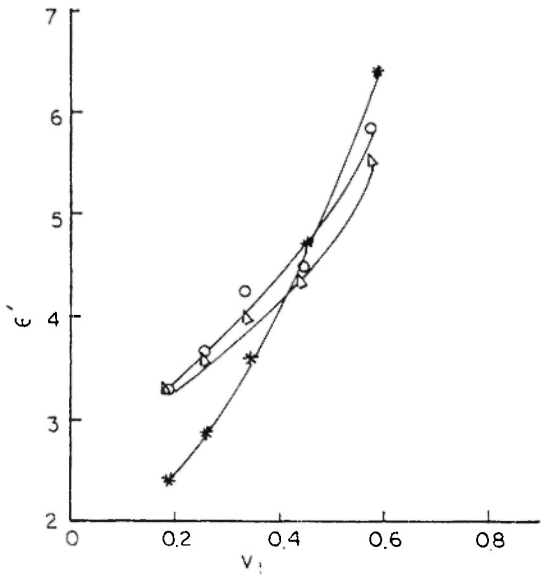

Fig. 9: Plots of theoretical and experimental dielectric constant vs. composition (volume fraction of alumina), O - Experimental, Δ - Theoretical (Maxwell-Wagner), * - Theoretical (Bottcher Bruggeman).

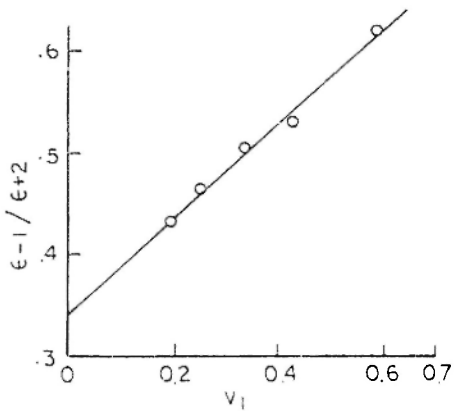

Fig. 10: Plot of specific polarization vs. composition (volume fraction of alumina).

= 0.457, i.e. x_1 = 70 wt.%. In general, the MW equation is applicable to a low concentration of a dispersed component in a continuous matrix and it considers dispersed particles to be spherical in nature, whereas the BB formula provides a good description of permittivities for a more concentrated mixture, especially when the permittivity ratio $\varepsilon'_1/\varepsilon'_2$ = 10, and all possible interactions between matrix and filler were admitted in this theory. This reflects that the interaction between PS and alumina is predominantly less above 70 wt.% alumina content. Finally, the plot of specific polarisation $(\varepsilon' - 1)/(\varepsilon' + 2)$ vs. v_1 (Fig. 10) is found to be linear with a unity slope and intercept = 0.345 (i.e. when v_1 = 0), as expected in accordance with Clausius-Mossotti's equation, modified by Lorenz and Lorentz for overall nonpolar dielectrics /8/.

CONCLUSION

It may be concluded that graded dielectrics can be obtained from PS - Al_2O_3 composites which can function as fruitful and lossy dielectrics for both electronic and radar devices. The systems conform to Lichteneker-Rother's logarithmic equation /5/ for heterogeneous dielectrics and also Clausius-Mossotti's equation for overall non-polar dielectrics.

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