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Modeling and Simulation of Artificial Core-Shell Based Nanodielectrics for Electrostatic Capacitors Applications

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Abstract: The need for high storage capacitors led to the development of polymer based capacitors. Polymers have high processability, mechanical flexibility, electrical breakdown strength and compatibility with printed circuit board (PCB) technologies but usually have very low permittivity (K). The permittivity of the polymer as well as its dielectric strength can be tuned to desired characteristics by introducing metallic nano fillers. In the 2010 COMSOL Multiphysics conference, we presented characteristics of capacitors fabricated with Au (core) and SiO_2 (shell) nano composites, dispersed in Polyvinyl Pyrrolidine (PVP) polymer solution. Effective Medium Theories (EMT) of Maxwell-Garnett, Bruggeman and Looyenga models were employed to calculate K value. It was found that with increase in volume loading of the Au nanofiller, K value of the composite increases. The dielectric permittivity of modified PVP increased from 7 to 1400 at percolation threshold using Au-SiO_2 core-shell nanoparticles. In this work, the Au nanoparticle and SiO_2 shell are replaced by silver (Ag) and polystyrene (PS) shell, respectively. The usage of polymer coating instead of SiO_2 cuts down a step in the preparation of core-shell nanoparticles, thus making the process simpler and cost effective. Removal of SiO_2 layer increases the polarization around the metallic core as a result of improvement in the acting electrical potential. This modification also leads to significant cost reduction in the fabrication process ingredients as Ag is less expensive than Au. Improved electrical performance can also be achieved, since Ag presents higher conductivity than Au. In COMSOL Multiphysics software, the AC/DC module is selected and the In-plane electric currents are applied to the physical model. The modified EMT is applied to the polymer core-shell to calculate the effective electrical properties of the composite. The percolation data analysis is used to predict the maximum theoretical K value of the composite and results of both 2D and 3D models under different amount of filler loading are presented.

Keywords: Nanodielectrics, Metal nano fillers, Polymer based capacitors, Effective Medium Theory, Percolation theory

1. Introduction

Extensive interest is being directed to the research on innovative nanodielectric materials because of their promising applications in energy storage solutions as both discrete and embedded capacitors. There is growing demand for capacitors that can store a lot amount of energy and deliver it instantaneously [1-3]. The polarizability of the dielectric plays an important role in the amount of charge stored. With increase in polarization, the electric field generated increases. Thus the charge storage or the capacitance increases as well.

1.1 Polymer Capacitors

Polymer capacitors have been used for energy storage for a long time. Polymers have high processability, mechanical flexibility, electrical breakdown strength, compatibility with printed circuit board (PCB) technologies and low equivalent series resistance. One major disadvantage of having polymer capacitors in that they usually have very low dielectric permittivity (K). The dielectric properties can be enhanced by inclusion of metal nano fillers, like Ag, Au, Ti, etc. Polystyrene is one of the efficient polymers for capacitors use, since it is readily soluble in all organic solvents.

1.2 Nano fillers

Noble metal nanoparticles is a domain in rapid expansion, as those objects lead to interesting applications in various fields. Because of their structure, intermediate between that of molecules and of bulk material, they enable to bridge the gap between molecular chemistry and surface science. In particular, their optical properties, known since

antiquity, have already shown part of their potential and further major discoveries can reasonably be expected [15]. Dramatic changes take place when the loading of these nano fillers in a polymer matrix reaches a particular threshold value, which is popularly called a percolation threshold [5].

1.3 FEM Simulation

To cut down on fabrication expenses, FEM analysis was applied to the design process to minimize the development time and predict the output patterns. With advancements in computer technology, simulation of complex percolative systems like nanodielectric capacitors has become a reality. The effective properties of the nano composites can be calculated using Finite element analysis, available in COMSOL multiphysics. Calculation of the effective permittivity in a metal polymer composite is the aim of this paper.

Effective properties of the composite can be calculated by modeling the permittivity using the Effective medium theory and generalized effective medium theory or other similar mean field theories [5]. The EMT utilizes various properties of the resultant medium such as shape, size, fraction of inclusions, individual dielectric permittivity, etc. to calculate the effective permittivity. The dielectric permittivity of Polystyrene is 2.6 [16]. The dielectric function of Silver, which is a noble metal, is calculated using the Drude-loretnz model. The fractions of inclusions were taken from a minimum of 0 to a maximum of 1.

The EMTs are generally valid only for low volume fractions. For higher fraction values, the effective properties can also be determined using Percolation theory [17]. However determining the percolation threshold is crucial in accurately predicting the properties using percolation theory [18]. The model of the nanocomposite is shown in figure 1.

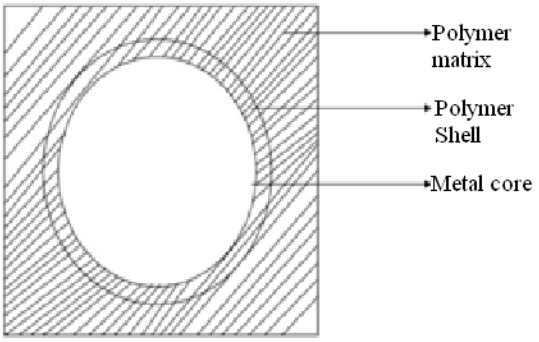


Figure 1. Model of the nano metal-polymer composite

2. Theoretical Framework

2.1 Drude Lorentz model

The dielectric function of any material can be decomposed into real term (ε') which determines the polarizability of the material in the presence of an electric field and the imaginary term (ε'') which determines the intrinsic loss mechanisms [13]. In the case of noble metals such as Ag, the dielectric function consists of two components, one is the Drude free electron term and the other is the substantial contribution of the bound or inter-band electrons [8-11]. Due to the additive nature of the dielectric function, it can be written as sum of both the components, as shown in equation 1.

$$\varepsilon_{bulk}(\omega) = \varepsilon_{free\text{-}electrons}(\omega) + \varepsilon_{inter\text{-}band\ electrons}(\omega) \quad (1)$$

In a bulk metal, the complex dielectric function, at frequencies from DC to ultra violet, is dominated by contributions from free electrons. In this region, the dielectric function has negative values. At bulk plasmon resonance frequency, ε will reach positive values. Metals are also characterized by inter band electron transitions, although they are important only at high frequencies. For one-metal electrons such as Ag, the inter band electron transition contribution is significant from optical to UV frequencies.

The complex dielectric function due to free electrons can be written as shown in equation 2.

$$\varepsilon_{free} = 1 - \frac{\omega_{pf}^2}{\omega^2 + i\omega\gamma_0} \quad (2)$$

where ω_{pf} is the plasma frequency, $1/\gamma_0 = T_0$ is the free electron scattering time, ω is the frequency.

Similarly, the dielectric function due to bound electrons can be written as shown in equation 3.

$$\varepsilon_{bound} = \frac{\omega_{pb}^2}{\omega_o^2 - \omega^2 - i\omega\gamma_b} \quad (3)$$

where ω_{pb} is the plasma frequency, ω_o is the bound electron resonant frequency, $1/\gamma_b = T_b$ is the bound electron decay time.

Therefore the bulk dielectric function of Silver can be written as,

$$\varepsilon_{bulk}(\omega) = 1 - \frac{\omega_{pf}^2}{\omega^2 + i\omega\gamma_0} + \frac{\omega_{pb}^2}{\omega_o^2 - \omega^2 - i\omega\gamma_b} \quad (4)$$

For metal particles smaller than their mean free path, decay time has been proved to be particle size dependent [8].

$$\gamma_f = \frac{1}{T_f} = \frac{1}{T_0} + 2\frac{V_f}{a} \quad (5)$$

where T_0 is the scattering time of the bulk material, V_f is the Fermi velocity, and a is the diameter of the particle. Thus the size dependence of the permittivity for a silver particle can be modified as

$$\varepsilon_{bulk}(a,\omega) = \varepsilon_{bulk}(\omega) + \frac{\omega_{pf}^2}{\omega^2 + i\omega\gamma_0} - \frac{\omega_{pf}^2}{\omega^2 + i\omega\gamma_f}$$

$$= 1 - \frac{\omega_{pf}^2}{\omega^2 + i\omega\gamma_f} + \frac{\omega_{pb}^2}{\omega_o^2 - \omega^2 - i\omega\gamma_b} \quad (6)$$

2.2 Effective Medium Theory

Effective medium theories are based on the fact that energy differences are easier to calculate than energies. The modus operandi goes as, "Choose a reference system with a known energy and concentrate on the energy difference" [9].EMTs and other mean-field like theories are physical models based on properties of individual components and their fractions in the composite [9]. Generally the properties that are calculated using EMTs are dielectric permittivity and conductivity. There are many EMTs, and each theory is more or less accurate under different conditions.

The most popular EMTs are:

Maxwell

$$\varepsilon_{eff} = \varepsilon_h + 3f\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}\varepsilon_h \quad (7)$$

Maxwell Garnet Model

$$\varepsilon_{eff} = \varepsilon_h\left[\frac{1 + 2f\left(\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}\right)}{1 - f\left(\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}\right)}\right] \quad (8)$$

Symmetric Bruggeman or Böttcher model

$$\varepsilon_{eff} = \frac{1}{4}[3f(\varepsilon_i - \varepsilon_h) + 2\varepsilon_i - \varepsilon_h + \sqrt{((1-3f)^2\varepsilon_i^2 + 2(2+9f-9f^2)\varepsilon_i\varepsilon_h + (3f-2)^2\varepsilon_h^2}] \quad (9)$$

Assymetric Bruggeman model

$$\frac{\varepsilon_i - \varepsilon_{eff}}{\varepsilon_i - \varepsilon_h} = (1-f)\left(\frac{\varepsilon_{eff}}{\varepsilon_h}\right)^{\frac{1}{A}} \quad (10)$$

And Loyenga Model

$$\varepsilon_{eff} = \left[\left(\varepsilon_i^{\frac{1}{A}} - \varepsilon_h^{\frac{1}{A}}\right)f + \varepsilon_h^{\frac{1}{A}}\right]^A \quad (11)$$

where ε_{eff} is the effective dielectric permittivity of the medium, f is the volume fraction of the filler, ε_i, ε_h are the dielectric permittivity of inclusions and host i.e. Ag and PS respectively. The term A, which is the depolarization factor, depends on the shape of the inclusions. The value of A is determined as 2 for disk fillers and 3 for spherical fillers.

2.3 Percolation theory

During the last five decades, percolation theory, an extensive mathematical model of percolation, has brought new understanding and techniques to a broad range of topics in physics, materials science, complex networks, and epidemiology as well as in geography. It allows prediction of the equilibrium state of large multicomponent systems through porous materials. Percolation theory takes into account the distribution of minor phase in the microstructure of the composite, which depends n its shape, size, and orientation. Percolation theory is one of the easiest mechanisms to model disordered systems because it has little statistical dependency; is an easy concept to realize even for the most complex systems, and its outcomes are realistic for qualitative predictions of random composites [17]. Percolation theory is significant when loading of minor phase of composite (fillers) reaches a critical value; at this critical value, substantial changes take place in the physical and electrical properties of

the system, sometimes on the order of more than a hundred times. This critical fraction of filler is called the percolation threshold, f_c. The abrupt changes in the properties of the system are particularly predominant if the components of the composite have large differences in their properties [18]. Ag has very high electrical conductivity of $63x10^6$ S/m and PS has very low electrical conductivity of $1x10^{-16}$. The significant difference between these two components makes percolation theory an ideal modeling tool.

A simple power law relation can be used to describe the changes in the properties in the system, near the percolation threshold [11].

$$\frac{K}{K_h} = |f - f_c|^{-s} \qquad (12)$$

where K is the effective dielectric permittivity, K_h is the dielectric permittivity of the host material, f is the fraction of inclusions and f_c is the fraction of inclusions at the percolation threshold and s is an exponent of value 1.

3. Use of COMSOL Multiphysics

In COMSOL Multiphysics, the AC/DC module is chosen as the Application Module. The Quasi-statics of conducting and dielectric materials with small currents in the plane and a negligible coupling between the electric and magnetic fields, is chosen as the sub module. This model was selected because it allows a frequency sweep to be conducted for different loadings of the inclusions at various frequencies.

3.1 Subdomain settings

The subdomain settings describe the physics on a model's main domain, which is divided into subdomains. You can set different values for each subdomain using settings of the following types:

- Coefficients that define the PDE on the subdomain. The PDE coefficients are available for PDE modes and the weak form modes.
- Material properties, sources, and sinks that define the physics in the subdomain, which are available in the COMSOL Module.

For convenience, we consider the second option, since the material properties can be easily determined. The thickness, dielectric permittivity and the electrical conductivity are set as the subdomain settings.

3.2 Boundary settings

The Boundary conditions define the interface between the model and its surroundings. In our case, we set one of the boundaries as port and set the forced voltage as input, which has a 1V value. The exact opposite boundary is set to ground. The other two boundaries are set to electrical insulation. Thus the whole setup makes the model look like a capacitor, with two metal plates with a dielectric in between. Figure 2 shown below, gives the schematic of the model boundaries.

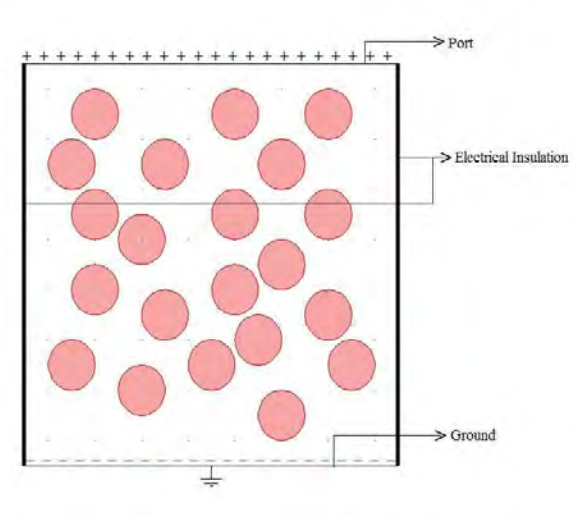


Figure 2. Boundary conditions

3.3 Simulation

Different geometries were drawn for different volume loading of the fillers keeping the dimensions of polymer matrix and nanofiller the same. Parametric sweeper was used to calculate effective properties for frequencies ranging from 1 KHz to 10 Peta Hz and a relative volumetric fractional loading of nanoparticles ranging from 0 to 1. Effective electrical properties such as the resultant electric field and resultant polarization were simulated and plotted using the post-processing feature in COMSOL Multiphysics. Effective dielectric permittivities up to the percolation threshold were calculated using the Effective Medium Theory equations.

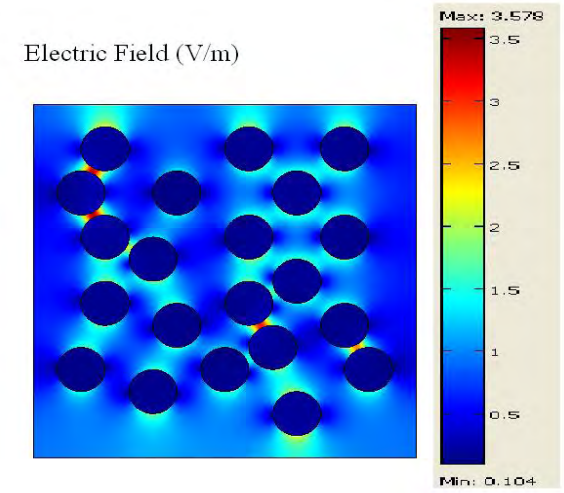
4. Results and Discussion

4.1 2D Modeling

The 2D model was drawn with the settings mentioned is section 3. A plot has been made for three different values of loading fractions, 0.134, 0.38 and 0.78 which corresponds to the number of Ag disks 11, 31 and 64 in a PS matrix with fixed thickness of 100nm. The radii of the Ag disks are considered to be 35nm.The electric field is generated in the dielectric in the presence of voltage applied using the boundary condition settings. In the presence of electric field, there are two polarizations acting on the medium. The first is the polarization of the PS matrix and the second one is the local polarization due to the Ag fillers. These two polarizations contribute to the net effective polarization. With an increase in net polarization, there is also increase in dielectric permittivity of the composite, which implies that the nano dielectrics with highest net polarization value have highest dielectric permittivity.

The increase in polarization, with increase in loading of the fillers f, is not linear. According to percolation theory, the dielectric permittivity increases only up to percolation threshold f_c, where it attains its highest value and then later on the dielectric permittivity starts decreasing. The value of the percolation threshold, f_c is not universal and depends on the structure of the dielectric [18]. For 2D modeling, the value of the percolation threshold was considered to be 0.785. The plot showing the electric field applied to different loading fractions are shown below.

3a



3b

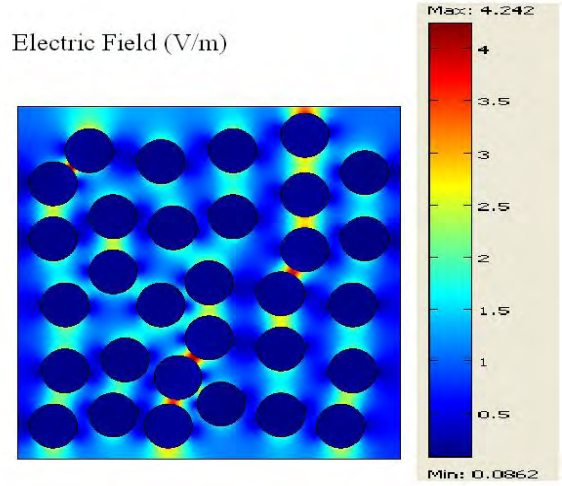
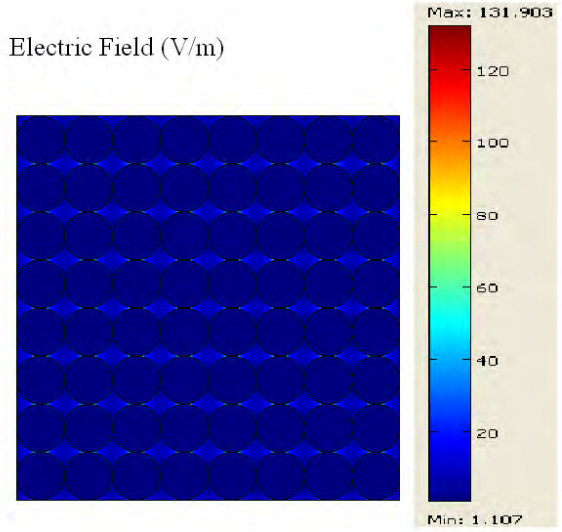


Figure 3. Electric field generated in the nanodielectric with a) f=0.134, b) 0.38, and c) 0.78, respectively.

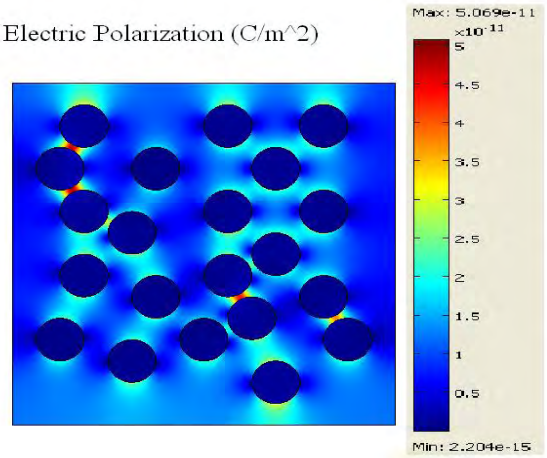
3c



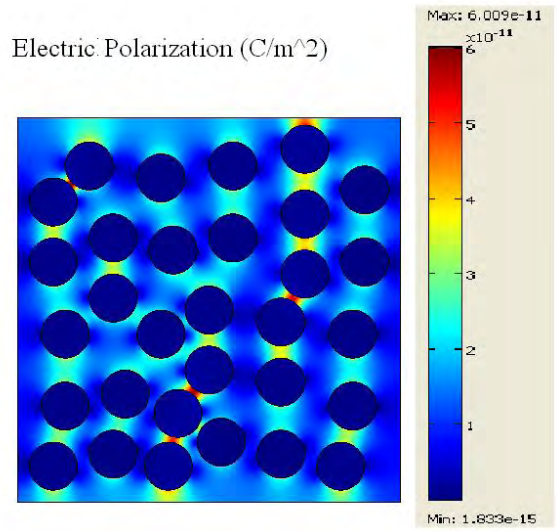
There is a gradual increase in the electric field with increase in the loading. The electric field is predominant near the places where there is transition from the polymer to the metal state. This is due to the exchange coupling between the metal and polymer. The exchange coupling is a short range force and hence the transition layers have highest electric field.

The highest value of electric field is obtained with fraction of loading 0.78, which is near the percolation threshold. The same pattern is observed in the case of polarization too. The plots showing the polarization for different loadings are shown in figure 4.

4a



4b



4c

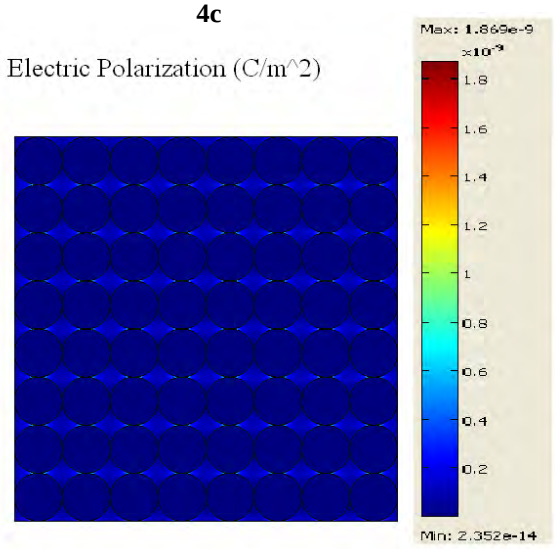


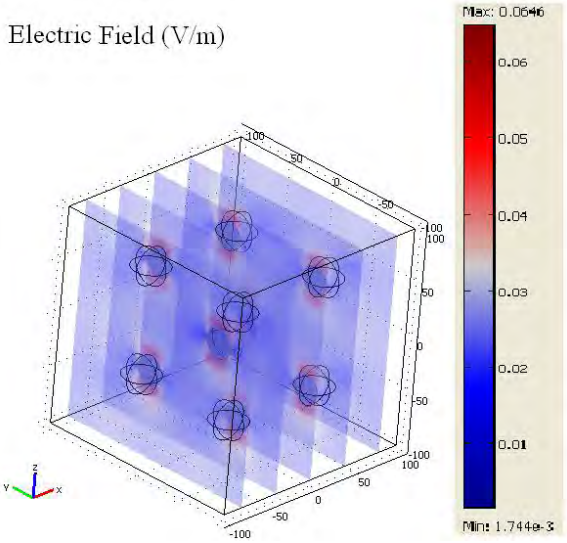
Figure 4: Electric polarization with a) f=0.14, b) 0.38, and c) 0.78, respectively.

4.3 3D Modeling

In order to determine the characteristics in 3D, three geometries were drawn with loading fractions of 0.022, 0.078 and 0.155 which corresponds to 8, 27 and 64 spheres. The same boundary and subdomain conditions mentioned in Section 3, apply to 3D modeling too. A value of 0.16, known as Sher-Zaller invariant [5] has been universally accepted as percolation threshold for a homogeneous composite with spherical fillers of the same size. We used the same value as our percolation threshold for our modeling.

The slice plots showing the electric field and polarization in the 3D domain have been drawn and shown in figure 5

5a



5b

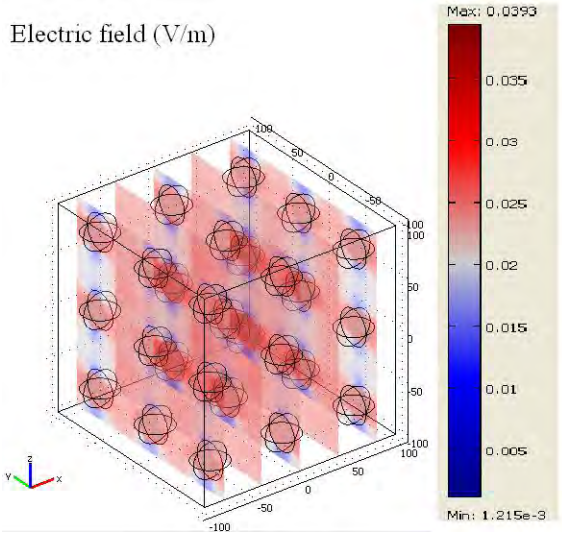


Figure 5. Electric field with a) f = 0.022 and b) 0.078, respectively.

5c

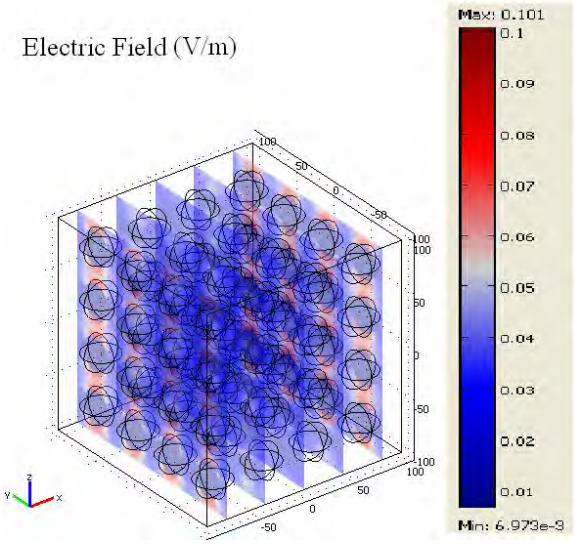


Figure 5c. Electric field with f = 0.155

5d

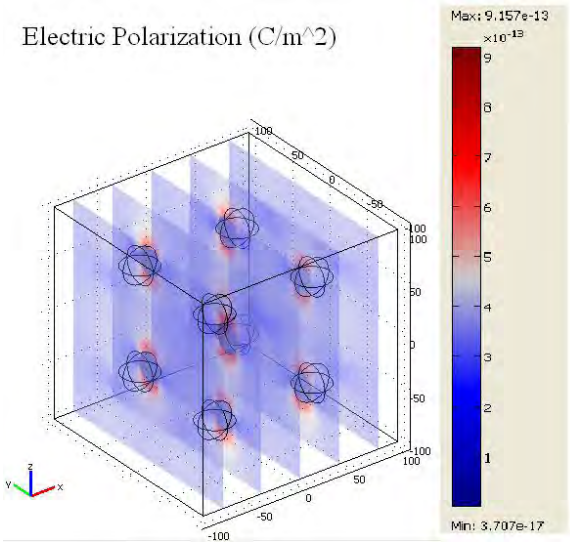
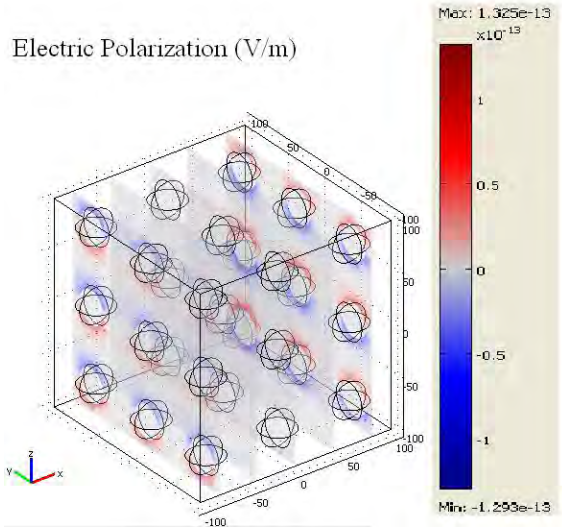


Figure 5d. Electric polarization with f = 0.022

5e



5f

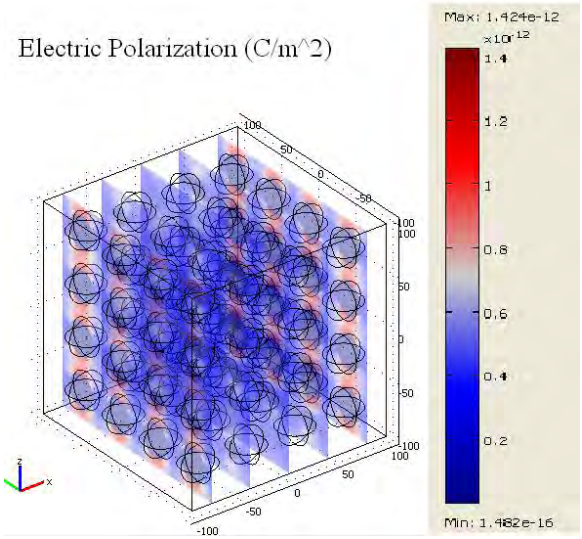


Figure 5. Electric Polarization with e) f = 0.078 and f) 0.155, respectively.

The net electrical field of the composite increases with loading, resulting in highest net polarization. The corresponding loading fraction is close to the percolation threshold. i.e., 0.16.

4.4 K calculation using EMTs

The K value of the medium is calculated using the effective medium theory equations described in section 2. Figure 6 shows the plot between the fraction of the nano filler and the dielectric permittivity calculated using different models.

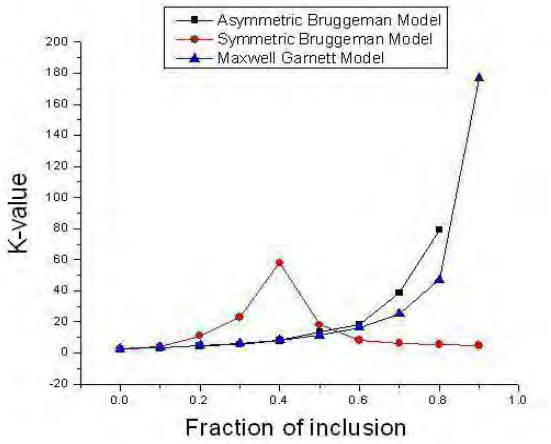


Figure 6. Graph plotted between K-value calculated using the 2D model and the Fraction of inclusion for various EMTs.

The frequency of operation is chosen as 1Ghz. Loyenga model is used in only cases when there is low contrast between the host and the inclusions. As There is a huge difference between Ag and PS and so it was not suitable to apply such model.

4.5 Percolation threshold

The value of K greatly depends on the amount of fillers. As mentioned previously, the K value increases with increase in the fraction of loading till the percolation threshold and then starts decreasing.

Figure 7 shows a plot of loading of nanofiller and dielectric permittivity of the composite calculated using the power low equation described in section 2.

7a

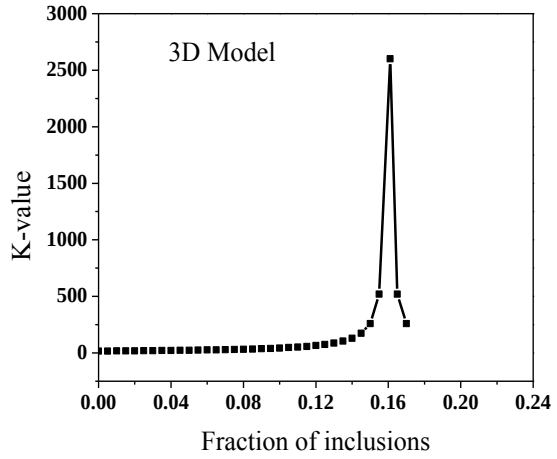


Figure 7a. Graph plotted between fractions of inclusions Vs K-value for 3D model.

7b

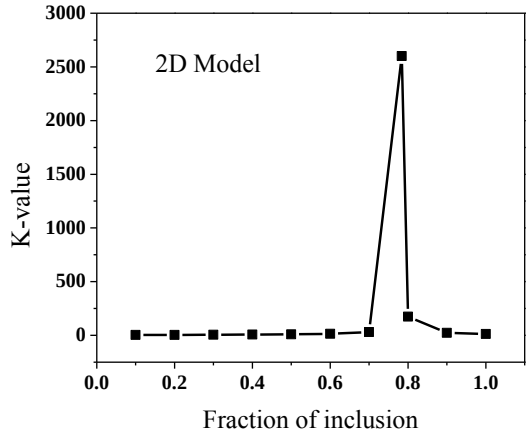


Figure 7b. Graph plotted between fraction of inclusions Vs K value for 2D model.

At zero loading, there are no nano fillers, which mean that there exists only the polymer. Hence we get the same K value as that of pure polymer. The K value increases as the loading increases and reaches a maximum of 0.784, which is close to the percolation threshold considered for our model. As the loading approaches to critical value, there is a significant increase in the dielectric permittivity, both in 2D and 3D models. If loading of nano fillers is increased beyond that, the complete polymer acts more or less like a conductor and hence the K value decreases.

5. Conclusion

The simulation model was successfully applied to planar capacitor structures with subdomain settings of both polymer and metal. The complex dielectric function of Silver was calculated using the Drude-Lorentz model. The electric field and the net polarization were found to increase with the metal loading. The study was undertaken for both the 2D and 3D models and electric field and polarization were plotted. The effective dielectric permittivity was calculated using the different EM theories including the Maxwell garnet model and the Symmetric and the asymmetric Bruggeman model. The percolation theory was then applied to find the K value for different loadings. A maximum dielectric permittivity of 2600 of the polystyrene-silver nanocomposite was achieved at the percolation threshold. This value is 1000 times higher when compared with pure polystyrene. The rapid increase in the effective dielectric permittivity was explained in light of the percolation and the Effective Medium theories.

6. References

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7. Appendix

Table 1: Various parameters used and their corresponding values

Parameter	Value	Reference
ω_{pf}, ω_{pb}	$2.17*10^{15}$ Hz	8
γ_b	$1.088*10^{14}$ Hz	8
ω_0	$7*10^{15}$ Hz	19
γ_0	$0.3*10^{14}$ Hz	8
V_f	$1.38*10^6$ m/s	19

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