Effective Medium Theory of Nanodielectrics for Embedded Energy Storage Capacitors

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Abstract: Extensive interest is being directed to the research of nanodielectrics because of its promising applications in energy storage solutions as both discrete and embedded capacitors. With increasing interest in the electromagnetic properties of nanodielectrics, it becomes crucial to analytically calculate the effective properties of the composite. Many theorists have developed effective medium theory (EMT) and other mean-field like theories to calculate the effective properties of macroscopically inhomogeneous medium. In this work, we present the effective properties of nanodielectrics with gold (Au) nanoparticles embedded in polymer (Polyvinyl Pyrrolidone (PVP)) matrix, calculated by using finite element method (FEM) based simulation in COMSOL Multiphysics software. Drude model is used to calculate size dependent complex dielectric function of Au. EMTs of Maxwell-Garnett, Bruggeman and Looyenga models are employed to calculate the effective permittivity of the composite and results are compared for 2D and 3D models. Nanodielectrics with metal fillers exhibit percolative behavior, which enhances the dielectric constant of the composite by many times at the percolation threshold. Through COMSOL simulations, we demonstrated an increase in dielectric constant value of PVP from 7 to 1400 at the percolation threshold using 35nm Au fillers.

Keywords: Nanodielectric, EMT, Drude model, Percolation, Nobel metal nanofillers.

1. Introduction

Storing of electrical energy is a key issue in all the present day electronic equipment. In particular, there is a growing demand for capacitors that can store a large amount of charge and deliver it instantaneously [1-3]. Amount of charge stored depends on the dielectric material used, which in turn depends on the polarizability of the dielectric. Greater the polarizability, greater the electric field generated and hence greater the charge storage or capacitance value.

1.1 Polymer Capacitors

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 dielectric constant (*K*). Dielectric and electrical properties of polymers can be tuned to desired characteristics by introducing fillers such as Au nanoparticles. Polyvinyl Pyrrolidone (PVP) is suitable for polymer matrix because it is readily soluble in water and many other organic solvents like Ethanol.

1.2 Nanofillers

Metal nanofillers have generated a great interest in recent times because of their fascinating physical and electrical properties. This type of nanoparticles belongs to a class of dielectric materials known as percolative composites. With an increase in volume loading of the nanofiller (Au), effective permittivity of the composite increases. Dramatic changes take place in the physical properties of the mixture as loading of the filler approaches percolation threshold of the composite [5]. Enhancement of dielectric constant of the composite in the vicinity of percolation threshold can be described by the widely popular power law [5,7].

1.3 FEM Simulation

With advancements in computer technology, simulation of complex percolative systems like nanodielectric capacitors has become a reality. Using the finite element method available in COMSOL Multiphysics, effective properties of the composites can be calculated. The primary goal here is to calculate the effective permittivity

of the composite medium formed by PVP and Au nanofillers. Effective permittivity can be modeled using effective medium theory (EMT) and Generalized Effective Medium Theory (GEMT) or similar mean-field like theories [4].

EMTs are used to calculate effective properties of the resultant medium by taking into account the size, shape, fraction and dielectric constant of both the fillers and the host matrix. Dielectric constant of Au is theoretically derived using the Drude-Lorentz model [8]. Dielectric constant of the polymer used in this work, PVP is experimentally determined as 7. Effective dielectric constant of the composite is calculated by varying the fractional loading of nanoparticles from 0 to a maximum value of 1.

EMTs are generally valid only for low-volume fraction of the inclusions. For metallic inclusions like Au nanoparticles, effective properties of the composite can also be determined using percolation theory as it is not hindered by a low-volume limit like EMTs. However, determining the percolation threshold is crucial in accurately predicting the properties using percolation theory.

2. Theoretical framework

2.1 Dielectric function of gold

Dielectric function of any material consists of a real term (ε') and an imaginary term (ε''). ε' determines the polarizability of a material in the presence of an electric field, and ε'' determines its intrinsic loss mechanisms [13]. For noble metals such as gold, complex dielectric function can be decomposed into two components [8-11]. One component is the Drude free-electron term, and the second component is the substantial contribution of the bound or inter-band electrons. Since the dielectric function is additive, it can be written as the sum of free electron and inter-band electron contributions [9] as written in Equation 1.

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

The complex dielectric function of inter-band electrons is calculated by taking into account the transitions between d-band and conduction sp-band electrons. Imaginary part of bound electron dielectric function arises from inter-band transitions, and the real part arises from polarizability of the bound d-band electrons of gold [11].The expression for dielectric function of bound electrons can be written using Lorentz oscillator model [8] as shown in Equation 2.

$$\varepsilon_{inter} = \frac{{\omega_{pb}}^2}{{\omega_0}^2-\omega^2-i\omega\gamma_b} \quad (2)$$

Where ω_{pb} is plasma frequency, ω_0 is bound-electron resonant frequency, $1/\gamma_b = T_b$ is the bound-electron decay time and ω is the frequency.

The complex dielectric function for the free electrons is given by Drude model [8,9] as in Equation 3.

$$\varepsilon_{free} = 1 - \frac{{\omega_{pf}}^2}{\omega^2+i\omega\gamma_0} \quad (3)$$

Where ω_{pf} is the plasma frequency and $1/\gamma_0 = T_0$ is the free-electron scattering time. Table 1 shows the values of all parameters used in this work and their references. Therefore, bulk dielectric constant of gold can be written as

$$\varepsilon_{bulk}(\omega) = 1 - \frac{{\omega_{pf}}^2}{\omega^2+i\omega\gamma_0} + \frac{{\omega_{pb}}^2}{{\omega_0}^2-\omega^2-i\omega\gamma_b} \quad (4)$$

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 Fermi velocity and a is the diameter of the particle. Through this modification, size dependencies of the gold particles are easily incorporated into its dielectric function expression [11] which can be written as

$$\varepsilon(a,\omega) = \varepsilon_{bulk}(\omega) + \frac{{\omega_{pf}}^2}{\omega^2+i\omega\gamma_0} - \frac{{\omega_{pf}}^2}{\omega^2+i\omega\gamma_f} = 1 - \frac{{\omega_{pf}}^2}{\omega^2+i\omega\gamma_f} + \frac{{\omega_{pb}}^2}{{\omega_0}^2-\omega^2-i\omega\gamma_b} \quad (6)$$

Where $\varepsilon(a,\omega)$ is the size dependent dielectric constant of a noble metal.

2.2 Effective Medium Theory

Effective medium theories (EMTs) are used to calculate the effective properties of a medium with inclusions. EMTs and other mean-field like theories are physical models based on properties of individual components and their fractions in the composite [4,12]. Generally the properties that are calculated using EMTs are dielectric constant and conductivity. There are many EMTs, and each theory is more or less accurate under different conditions.

Most popular EMTs [4,6] are those of Maxwell

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

Maxwell – Garnett 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 model (also termed as Böttcher)

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

Asymmetric 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 Looyenga 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 constant of the medium, f is the volume fraction of the filler, ε_i is dielectric constant of the Au filler, ε_h is dielectric constant of the host PVP matrix and A is a depolarization factor, which depends on the shape of inclusions. Value of A is 2 for disk fillers and 3 for spherical fillers.

2.3 Percolation

Percolation was originally studied as a mathematical subject but its broadest applications are found in the field of material research [5]. Percolation is one of the easiest mechanisms to model disordered system as it has very little statistical dependence. It is easy to realize the concept of percolation even for most complex systems and its outcomes are not unrealistic for qualitative predictions of random composites [14]. Percolation theory becomes significant when loading of minor phase of the composite (fillers) reaches a critical value. At this critical value, substantial changes take place in physical and electrical properties of the system, sometimes in order of more than hundred times. This critical fraction of filler is termed as percolation threshold, f_c. The abrupt changes in properties of the system are particularly predominant if the constituent components of the composite have a large difference in their properties. Au filler and PVP matrix considered in this work, have highly varying electrical properties. Au has a high conductivity of $45.2*10^6$ S-m^{-1} while PVP has a very low conductivity of $5.5*10^{-8}$ S-m^{-1}.

Simple power law expression describes the significant changes in properties of the system near the percolation threshold.

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

Where K is the dielectric constant of the composite, K_h is the dielectric constant of the matrix (PVP), f_c is percolation threshold, f is the filler volume fraction and s is an exponent of value about 1.

3. Use of COMSOL Multiphysics

In COMSOL Multiphysics, electrostatics - in plane electric current model was used to simulate the effective properties of nanofiller/polymer composite capacitors. This model was selected because it allows a frequency sweep to be conducted for different loadings of the nanofiller at different frequencies. In order to simulate the effective properties of the dielectric, electrical conductivity of the materials and their dielectric constants were used as sub domain conditions.

One of the boundaries was set to a port as the input voltage, while its opposite boundary was maintained at ground. All other boundaries were set to periodic continuity condition. This makes the geometry analogous to a parallel-plate capacitor with a voltage applied across its plates. 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 constant and dielectric constant at the percolation threshold were calculated using the equations mentioned in section 2.

4. Results and Discussion

4.1 Dielectric constant of gold

Size dependent dielectric constant of Au is calculated from Equation 6. In this work, we considered Au nanofillers of 35nm diameter. Scattering time and damping factor of 35nm gold particle were calculated using Equation 5 and their values were obtained as $3.77*10^{-14}$ seconds and $2.65*10^{14}$ Hz, respectively. Figure 1 shows the plot between real and imaginary parts of the dielectric constant of gold with varying frequency.

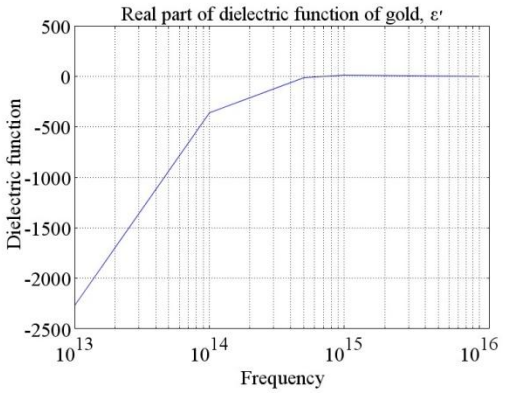


Figure 1(a): The real part of dielectric function of gold Vs frequency.

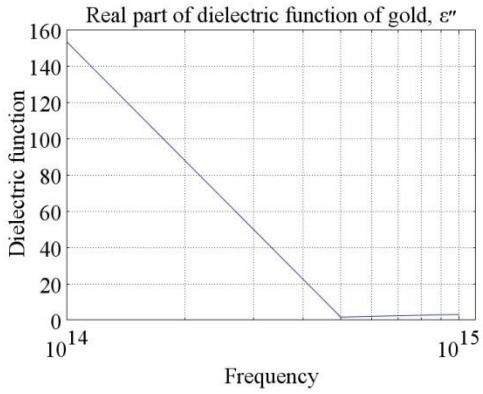


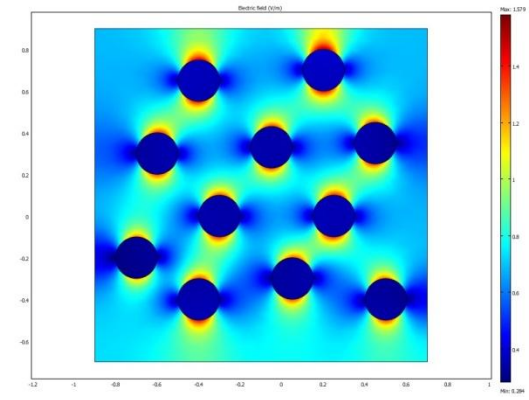
Figure 1(b): The imaginary part of dielectric function of gold Vs frequency.

4.2 2D modeling

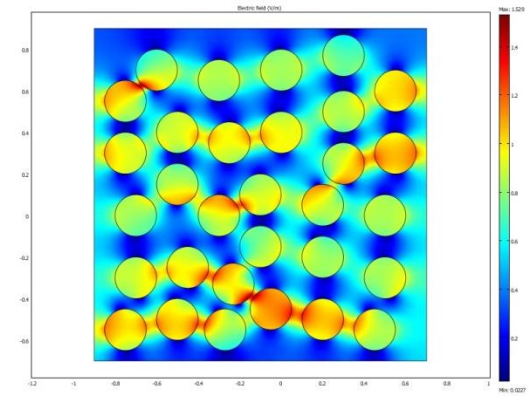
To perform 2D modeling, geometries were drawn to represent nanodielectric with 3 different volume fractions: *f* value of 0.134, 0.38 and 0.78 corresponds to nanodielectrics with random arrangement of 11, 31 and 64 Au disks in a PVP matrix of fixed dimension. Electric field is generated in the dielectric in the presence of a voltage applied using aforementioned sub-domain and boundary conditions. In the presence of an electric field, apart from polarization of the PVP matrix, local polarization is generated at the surface of nanofillers because of the presence of bound electrons of Au. Local polarization from all the fillers is added which contributes to the increase in net polarization of the nanodielectric. With an increase in net polarization, there is also an increase in dielectric constant of the composite. Therefore, nanodielectrics with the highest net polarization value have highest dielectric constant.

However, this increase in polarization is not linear with the increase in loading of nanofiller. According to percolation theory, it increases till loading of nanoparticles reaches the percolation threshold, f_c and rapidly decreases with further increase in loading. The quantity f_c is non-universal and strongly depends on the structure of the nanodielectric. This is discussed in detail using examples mentioned in the section below. For 2D modeling, an f_c value of 0.785 was considered for our work.

(a)



(b)



(c)

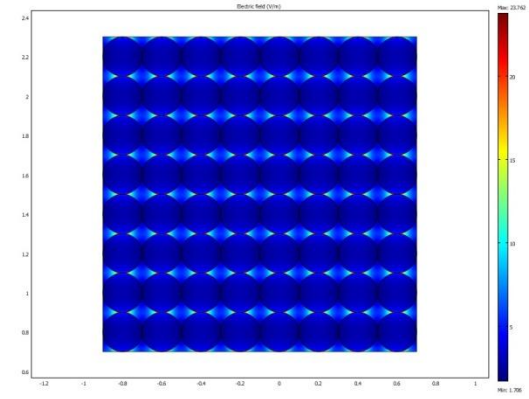
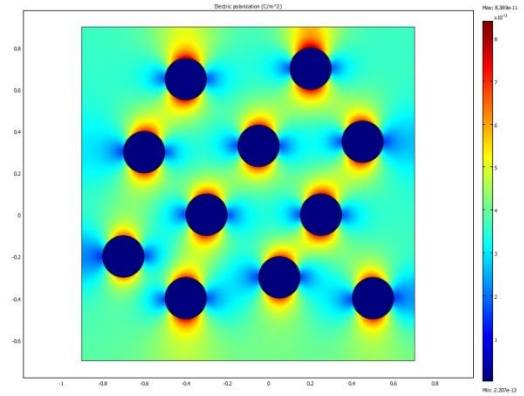


Figure 2(a), (b) and (c): Electric field generated in the nanodielectric with,(a) f=0.134, (b) f=0.38 and (c) f=0.78 respectively.

Enhancement of electric field, and hence the polarization, at the surface of filler is clearly observed. From the above images, it is evident that with an increase in filler volume fraction, there is an increase in net electric field. Even in case of low-volume fraction of the filler, particles with closer vicinity can have much enhanced electric field between them, but net enhancement of the electric field is greater for dielectric with more loading of nanoparticles. Highest electric field is observed at the surface of the fillers in dielectric with volume fraction of 0.78, closest to the percolation threshold.

The same phenomenon is observed in the polarization patterns of all loadings of the nanodielectric samples as shown in figure 3. Highest polarization is observed in dielectric with f=0.78 and least in f=0.134. Figure 3 illustrates the polarization pattern in all the 3 different loadings of nanodielectrics.

(a)



(b)

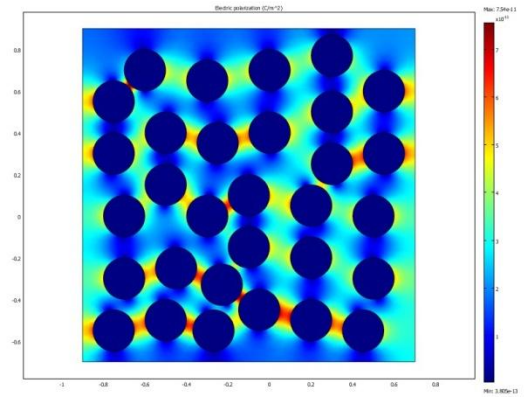


Figure 3 (a) and (b): Electric polarization in the nanodielectric for (a) f=0.134 and (b) f=0.38 respectively.

(c)

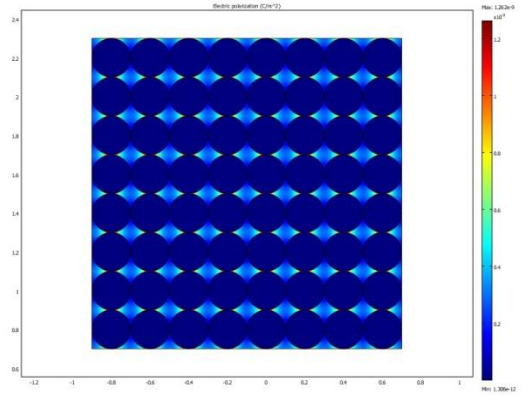


Figure 3 (c) Electric polarization in the nanodielectric with f=0.78.

4.3 3D modeling

To study the 3D modeling of nanodielectric, 3 geometries were drawn with arrangement of 8, 27 and 64 spheres having a volume fraction of 0.022, 0.078 and 0.155, respectively. 2D and 3D models are essentially the same with a difference that disks are replaced with spheres. The electric field and polarization patterns of the dielectric mentioned in section 4.2 holds true for 3D modeling as well. 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. In this work, we assume a percolation threshold value of 0.16 for 3D modeling.

(a)

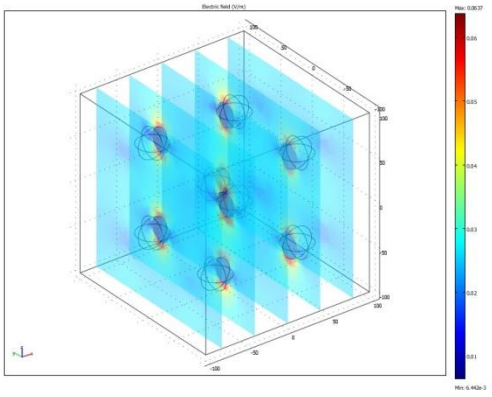
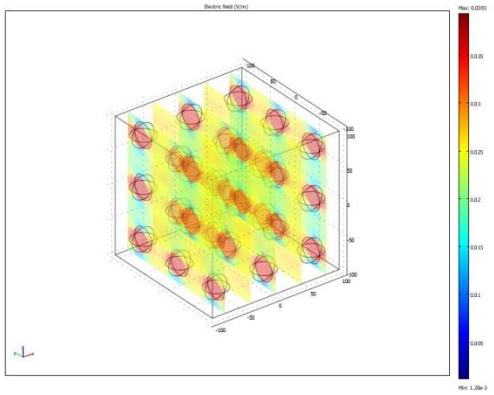


Figure 4(a): Electric field generated in nanodielectric with f=0.022.

(b)



(c)

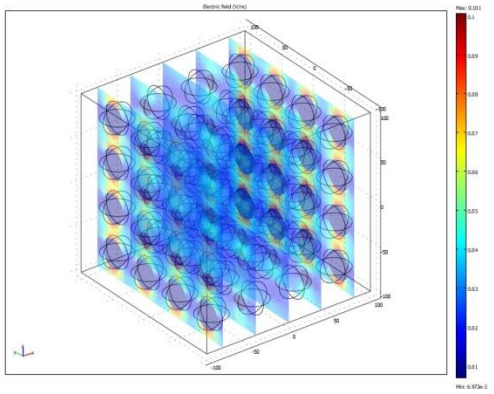


Figure 4 (b) and (c): Electric field generated in nanodielectric with f=0.078 and f=0.155 respectively.

Figure 4 shows the slice plots of electric field distribution in the 3D dielectrics with nanofillers of fraction 0.022, 0.078 and 0.155. Highest enhancement of the electric field is observed in the samples with loading closest to the percolation threshold.

Net polarization of all loadings of nanodielectrics can be expected to follow the same pattern as the electric field. Figure 5 shows polarization at the fillers and in the polymer matrix for all 3 filling concentrations. Nanodielectric with filler concentration close to the percolation threshold witnesses the highest net polarization, which implies that it has the highest dielectric constant.

(a)

(b)

(c)

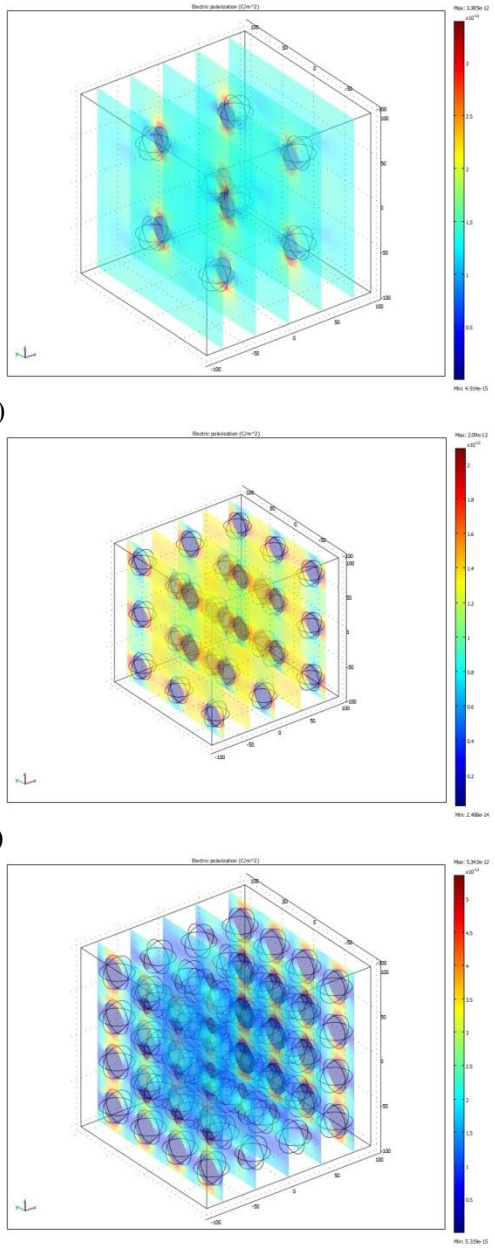


Figure 5 (a), (b) and (c): Electric polarization in the 3D nanodielectric for (a) f=0.022, (b) f=0.078 and (c) f=0.155 respectively.

4.4 *K* calculation using EMTs

Dielectric constant of the medium can also be calculated using effective medium theories mentioned in section 2. Figure 6 is a plot between the fraction of nanofiller and dielectric constant of the composite calculated using Maxwell-Garnett and Bruggeman symmetric and asymmetric models.

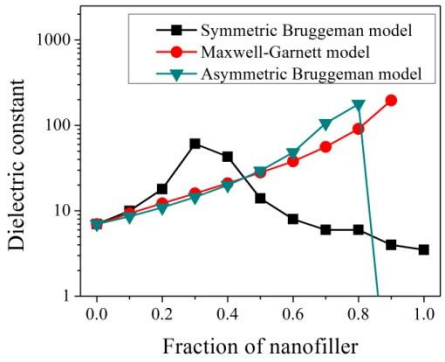


Figure 6: Real part of dielectric function of 2D composite calculated through various EMTs at 1GHz.

The above plot shows a comparison between the EMT models for Au filler in a PVP matrix. All models give almost the same value of dielectric constant in the low-volume fraction limit. Looyenga model is valid only if there is a low-contrast between the filler and matrix. However, in the case of metallic filler embedded in polymer matrix, there is a huge contrast between the properties of these two constituents. This makes Looyenga model unsuitable for this work.

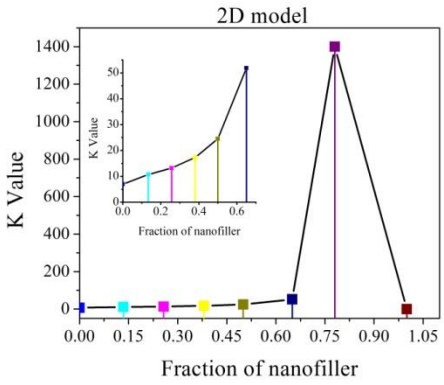
4.5 *K* at percolation threshold

The technique of preparing percolative composites to increase dielectric constant of the polymer- based capacitors greatly depends on the concentration of the nanofiller. As mentioned earlier, *K* value of composites can be dramatically increased when loading of the nanofillers is in the vicinity of the percolation threshold. In this work, we noticed a two hundred times increase in dielectric constant of PVP matrix when loading of nanoparticle is near the percolation threshold.

Figure 7 is a plot between loading of nanofiller and dielectric constant of the composite calculated using Equation 12. Fraction of nanofillers and K values of the composite are calculated separately for the above mentioned 2D and 3D models. From graphs 7(a) and 7(b), it can be inferred that dielectric constant of the

composite increases gradually with an increase in loading of nanofillers and reaches a value of 1400 at the percolation threshold. At zero loading of nanofillers, the dielectric constant of the composite is same as dielectric constant of the polymer itself.

(a)



(b)

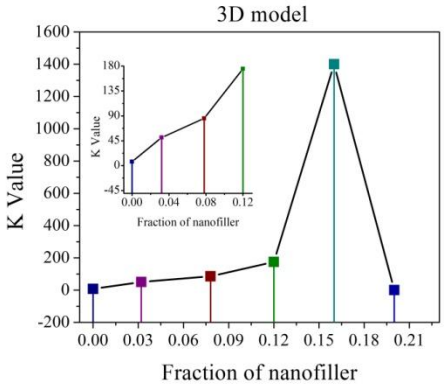


Figure 7 (a): Graph plotted between Dielectric constant Vs fraction of filler for above mentioned 2D models and (b) 3D model respectively.

Inset pictures in graphs 7 (a) and 7 (b) show the gradual increase in K value with the increase in loading of nanofillers. As the loading approaches the critical value of the percolation threshold, there is a significant increase in dielectric constant of the composite, as noted in both 2D and 3D models. If loading of nanofillers is increased beyond percolation threshold, composite becomes conductive in nature. This leads to a rapid fall in the dielectric constant.

5. Conclusion

Complex dielectric constant of gold is calculated using Drude-Lorentz model. Enhancement of local and net polarization, electric field is observed with increasing loading of nanoparticles in polymer till percolation threshold is reached. The above case is studied for both 2D and 3D models, and graphs were plotted to explain the phenomenon of percolation. Significant increase in dielectric constant of the composite (1400) is achieved when compared to dielectric constant of bare polymer (7) by introducing 35nm sized Au nanoparticles. Effective dielectric constant of the composite was also calculated using EMTs of Maxwell-Garnett, symmetric Bruggeman and asymmetric Bruggeman. Like the percolation theory, EMTs also predict an increasing trend of dielectric constant with an increase in volume fraction of the filler. The dielectric constant values calculated using EMTs and percolation theory are in close range when loading of the nanofillers is low. But EMTs failed to predict the rapid increase in dielectric constant of the composite at the critical concentration of fillers, f_c.

6. References

1. J. Lu and C. P.Wong, "Recent advances in high-k nancomposite materials for embedded capacitor application," IEEE Trans. Dielectr. Electr. Insul.,vol. 15, no. 2, pp. 1322–1328, Oct. 2008.
2. J. Y. Li, L. Zhang, and S. Duchame, "Electric energy density of dielectric nanocomposites", Appl. Phys. Lett. 90, 132901, 2007.
3. S. K. Saha, "Nanodielectrics with giant permittivity", Bull. Mater. Sci., Vol. 31, No. 3, June 2008, pp. 473–477.
4. V. Myrochnychenko and C. Brosseau, "Finite-element method for calculation of the effective permittivity of random inhomogeneous media", Physical Review E 71, 016701, 2005.
5. C. W. Nan, Y. Shen and Jing Ma, "Physical properties of composites near percolation", Annu. Rev. Mater. Res. 2010. 40:3.1–3.21
6. William M. Merrill, et al, "Effective Medium Theories for Artificial Materials

Composed of Multiple Sizes of Spherical Inclusions in a Host Continuum", IEEE Transactions on antennas and propagation, vol. 47, no. 1, January 1999.
7. Yang Shen et al, "High Dielectric Performance of Polymer Composite Films Induced by a Percolating Interparticle Barrier Layer", Adv. Mater. 2007, 19, 1418–1422.
8. A. E. Neeves and M.N.Birnboim, "Composite Structure for the enhancement of nonlinear-optical susceptibility", J.Opt Soc. Am. B. Vol 6, No. 4, April 1989.
9. Lucia B Scaffardi and Jorge O Tocho, "Size dependence of refractive index of gold nanoparticles", Institute Of Physics Publishing, Nanotechnology, 17, 1309–1315, 2006.
10. U. Kreibig and M. Vollmer, "Optical properties of metal clusters", Springer, Springer series in materials science, 25, 1995.
11. R. D. Averitt, D. Sarkar, and N. J. Halas, "Plasmon Resonance Shifts of Au-Coated Au2S Nanoshells: Insight into Multicomponent Nanoparticle Growth", Phys Rev Lett, Vol 78 No 22, June 1997.
12. Tuck C. Choy, "Effective medium theory – principles and applications", International series of monographs on Physics, Oxford science publications, 1999.
13. N.K. Grady, N.J. Halas, P. Nordlander, "Influence of dielectric function properties on the optical response of plasmon resonant metallic nanoparticles", Chemical Physics Letters 399, 167-171, 2004.
14. Geoffrey Grimmett, "Percolation", Springer link, 1991.

7. Appendix

Table 1: Parameters used to calculate dielectric constant of gold:

Parameter	Value	Reference
ω_{pf}, ω_{pb}	$1.38*10^{-16}$ Hz	8
Υ_b	$2.4*10^{14}$ Hz	9
ω_0	$7*10^{15}$ Hz	8
Υ_0	$1.1*10^{14}$ Hz	9
V_f	$1.38*10^{6}$ m/sec	8