Modeling and Simulation of High Permittivity Core-shell Ferroelectric Polymers for Energy Storage Solutions

Rakesh Mekala[1], Nacer Badi*[1,2]

[1]Center for Advanced Materials, University of Houston, Houston, TX77204-5004
[2]Department of Physics, University of Houston, Houston, TX77204-5005
*Email address of corresponding author: nbadi@uh.edu

Abstract: Extensive interest is being invested into the research of polymer based nanodielectrics. Such materials provide more practical energy storage solutions primarily for embedded capacitors. Polymer embedded metal nanofiller is considered as a great choice to achieve the above stated high energy storage. Our earlier simulation work reported that capacitors fabricated with dielectrics consisting of Au core and SiO_2 shell nanocomposite dispersed in Polyvinyl Pyrrolidine (PVP) polymer solution, showed a maximum electrical permittivity K of 2600 at 10kHz with 0.16% nanoparticles loading [1]. The K values were calculated using effective medium theories (EMT) of Maxwell-Garnett, Bruggeman and Looyenga models. However, the experimental findings with similar loading showed relatively very low K values. This is because the simulation results were based on highly ordered nanoparticles in the polymer matrix, a configuration which is quite difficult to achieve experimentally. We propose to narrow this discrepancy in the results by developing nanodielectric films based on embedding highly ferroelectric Polyvinilydine fluoride (PVDF) polymer matrix with high conductivity aluminum (Al) cores and solid aluminum oxide (Al_2O_3) as capping shells for electrical insulation and simulate the system considering less ordered nanoparticles in polymer matrix to feedback the experimental work. This approach is simple, cost effective and employs a polymer which is chemically inert to most solvents. It is also a low-smoke generation material during a fire event which makes it highly desirable to use in embedded capacitor applications. Apart from the above features, PVDF is highly ferroelectric which adds up in further enhancing the dielectric response at lower applied electrical fields with a minimum amount of nanoparticle loading. 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 with equations representing the ferroelectric nature of the polymer is applied to the polymer based 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 nanocomposite and results of 3D models under different amount of filler loading are presented.

Keywords: Nanodielectrics, energy storage, PVDF, core-shell nanoparticles, embedded capacitors

1. Introduction

Every generation of capacitors are primarily credited to the innovation and engineering of new dielectric materials. High electrical permittivity (K) materials have received tremendous interest recently due to their potential applications in energy storage solutions for electronic equipment. In particular, there is a growing demand for capacitors that can store a large amount of charge and deliver it instantaneously. Such storage capacity depends on the type of materials and polarizability (dipole moment orientation) of the said dielectric materials. This polarizability property can be further enhanced by adding nanoparticles to the matrix of polymeric material that can also greatly improve the thermal, mechanical and other electrical properties of the nanocomposites.

1.1 Metal filled polymer composite

Polymer composites filled with metal are of interest for many fields of engineering. This interest arises from the fact that the electrical characteristics of such composites are close to the properties of metals, whereas the mechanical properties and processing methods are typical for plastics [1]. The influence of the type of polymer matrix and filler on the electrical characteristics of the composite mainly depends on the percolation threshold. This composite overcomes the

disadvantage of high loading required for ceramic fillers but direct contact of conductive fillers will result in a high dielectric loss. This might also form a conductive path in the polymer composites. Therefore, a core-shell structure is proposed for nanofillers, in which an insulating shell is coated around each conducting filler. Non-conductive shells act as inter-particle barriers and prevent the conductive cores from coming in contact with each other during the dispersion process. Core/shell structured nanoparticles can be synthesized using methods such as coating a non-conductive shell on conducting filler. Our approach is to oxidize a conductive metal core to form a non- conductive metal oxide shell around it. Core-shell filler/polymer composites are expected to have high *K* values because of the increase in net polarization of the dielectric. They will also have low loss tangents due to non-conductive shell.

1.2 PVDF Polymer embedded nanoparticles

PVDF is now being considered as a great candidate for polymer nano-composites as it has amazing qualities - it is highly non-reactive to solvents, acids, bases. It is a low-smoke generation material during a fire event and it has a low density (1.78g/cm^3) and low cost compared to the other fluoropolymers. Apart from the above features it is highly ferroelectric which further helps in enhancing the dielectric response at lower electrical fields with a minimum amount of nanoparticle loading. In this paper, we will describe the use of PVDF as a polymer matrix for producing high electrical permittivity (K) material using Al_2O_3 shells coated Al metal nanoparticles.

1.3 FEM Simulation

Finite element method (FEM), often known as finite element analysis (FEA), is a numerical technique used to find approximate solutions of partial differential and integral equations arising from engineering and physics problems FEM requires a problem to be defined in geometry and subdivided into a number of symmetrical identities called as mesh elements.

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 [2]. 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 complex dielectric permittivity of PVDF is calculated using the Drude theory and the one for the metal is calculated using Drude-Lorentz model. The fractions of inclusions were taken from a minimum of 0 to a maximum of 1.

Percolation theory helps in determining the system behavior near percolation threshold, which is the essential characteristic of the system, and it is studied using a simple power law expression.

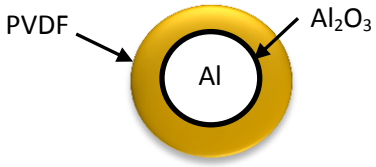

Fig.1: Model of nano-metal/polymer composite.

2. Background theory

2.1 Drude theory

THEORY OF DIELECTRIC BEHAVIOR

Debye [3] gave the classical picture of relaxation of polarization with a single relaxation time in a dielectric material. In his work he considered a set of non-interacting dipoles free to rotate in opposition to some viscous resistance in a fluid like medium. The equation for complex permittivity is:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} \qquad (1)$$

Where ε_0 = Electrical permittivity at low frequency
ε_∞ = Electrical permittivity at high frequency
ω = Angular frequency
τ = Relaxation time

According to Frohlich, the real and imaginary parts of the electrical permittivity are given by:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \quad , \quad \varepsilon'' = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau}(\omega\tau) \qquad (2)$$

ε' determines the polarizability of a material in the presence of an electric field, and ε'' determines its intrinsic loss mechanisms [4].

2.2 Drude Lorentz model

For metals such as aluminum, complex dielectric function can be decomposed into two components [5-6]. 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 [7] as in Equation 3.

$$\varepsilon_{bulk}(\omega) = \varepsilon_{free-electrons}(\omega) + \varepsilon_{inter-band\ electrons}(\omega) \quad (3)$$

The complex dielectric function of inter-band electrons is calculated by taking into account transitions between d electrons and conduction sp-band electrons. The 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 aluminum [6]. The expression for the dielectric function of bound electrons can be written using Lorentz oscillator model [5] as shown in Equation 4.

$$\varepsilon_{\text{int}} = \frac{\omega_{pb}^{\ 2}}{\omega_0^{\ 2} - \omega^2 - i\omega\gamma_b} \quad (4)$$

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

The complex dielectric function for the free electrons is given by Drude model [5, 7] as in Equation 5.

$$\varepsilon_{free} = 1 - \frac{\omega_{pf}^{\ 2}}{\omega^2 + i\omega\gamma_0} \quad (5)$$

Where ω_{pf} is the free electron plasma frequency and $1/\gamma 0 = T_0$ is the free-electron scattering time. Therefore, bulk electrical permittivity of aluminum can be written as:

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

For metal particles smaller than their mean free path, decay time has been proved to be particle-size dependent [5].

$$\gamma_f = \frac{1}{T_0} + \frac{2v_f}{a} \quad (7)$$

V_f is Fermi velocity and d is the diameter of the particle. Through this modification, size dependencies of the aluminum particles are easily incorporated into its dielectric function expression, which can be written [6] as:

$$\varepsilon_{(a,w)} = 1 - \frac{w_{pf}^{\ 2}}{\omega^2 + i\omega\gamma_f} + \frac{\omega_{pb}^{\ 2}}{\omega_0^{\ 2} - \omega^2 - i\omega\gamma_b} \quad (8)$$

Where $\varepsilon(a,\omega)$ is the size dependent electrical permittivity of a metal.

2.3 Effective Medium Theory

Effective medium theories are based on the fact that energy differences are easier to calculate than energies. 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. Most popular EMTs [4, 6] are Maxwell – Garnett model:

$$\varepsilon_{eff} = \varepsilon_h + 3f\left(\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}\right)\varepsilon_h \quad (9)$$

Symmetric Bruggeman model:

$$\varepsilon_{eff} = \frac{1}{4}[3f(\varepsilon_i - \varepsilon_h) + 2\varepsilon_h - \varepsilon_i + \sqrt{(1-3f^2)\varepsilon_i^{\ 2} + 2(2+9f-9f^2)\varepsilon_i\varepsilon_h + (3f-2)^2\varepsilon_h^{\ 2}}] \quad (10)$$

Looyenga model:

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

Where ε_{eff} is the effective electrical permittivity of the medium, f is the volume fraction of the filler, ε_i is electrical permittivity of the Au filler, ε_h is electrical permittivity of the host PVP matrix and A is a depolarization factor, which depends on the shape of inclusions. Value of A is 3 for spherical fillers.

2.3 Percolation theory

Percolation theory takes into account the distribution of minor phase in the microstructure of the composite, which depends on 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 [9]. Percolation theory is significant when loading of minor phase of composite (fillers) reaches a critical value at which substantial changes take place in the 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 aluminum/PVDF (electrical conductivity) gives us good benchmark to use the percolation theory. A simple power law relation [10] can be used to describe the changes in the system properties near the percolation threshold.

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

Where K is the effective dielectric permittivity, K_h is the dielectric permittivity of the host PVDF 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 for metal fillers.

3. Use of COMSOL Multiphysics®

Effective properties of the nanocomposites can be calculated using COMSOL Multiphysics®, a finite element method (FEM) based simulation software. The primary goal of simulation in this research is to calculate the effective permittivity of the composite medium formed by PVDF and Al_2O_3 core-shell nanoparticles. Effective permittivity can be modeled using percolation theory and effective medium theories (EMT). In plane electric current model was used to simulate the effective properties of nanofiller/polymer dielectric composite capacitors.

a) Creating geometry

First step towards a successful FEM simulation is to create a geometry that is most suitable to the problem being solved. Geometries needed for simulation of the composite nanodielectric environment are drawn in 3D models with varying filler fractions. Each loading fraction in either model is created as a separate file with an independent geometry.

Figure 2 shows the geometry setup of 3D model nanodielectric embedded core-shell nanoparticles with spherical disks of core radius 35nm and shell radius 45nm that are enclosed in a rectangular block of fixed area that defines the PVDF polymer matrix. The location of different nanoparticle is randomly generated by using a MATLAB function and the corresponding geometry is built in COMSOL software®.

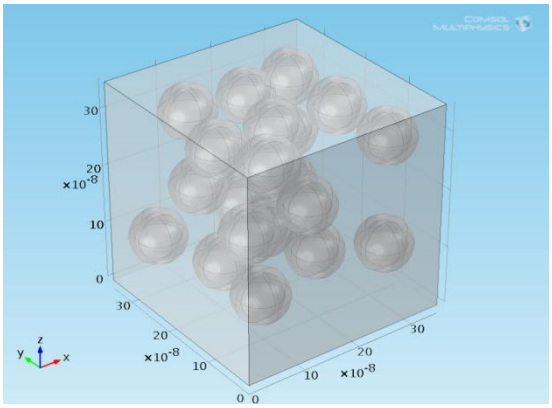

Fig.2 Polymer matrix with randomly dispersed nanoparticles.

b) Setting the model

In COMSOL Multiphysics®, Electrostatics – in-plane electric current module was used to simulate the effective properties of $Al@Al_2O_3$ core-shell nanofiller/PVDF composite capacitors. This module was selected because it allows a frequency sweep to be conducted for different loadings of the nanofiller at different frequencies. In sub-domain settings, there is a provision to choose the basic governing equation; polarization P which is directly proportional to the applied electric field E is given by: $P= \varepsilon_o *(\varepsilon_r-1)*E$ of the composite, which are the major concepts of the governing physics of metal-insulator composite nanodielectric capacitors. Therefore, these concepts are primarily considered in the analysis of simulation results.

After the geometry is drawn, each section of it is assigned to appropriate materials using sub-domain settings. In a 3D geometry, top face is set to the port where input alternating voltage (sine function is considered in simulations with unit amplitude) is applied, while its opposite face is maintained at ground. The remaining sides are maintained at periodic condition. This makes the geometry analogous to a parallel-plate capacitor with a voltage applied across its plates.

c) Solving the model

The final step before simulating the model after creating the geometry, declaring its physical properties and defining its guiding equations and constants, is setting the variables. For this, a parametric solver is used in COMSOL Multiphysics®. The solution is obtained from simulations by setting the variables and their possible values through parametric solver. This completes the model building after which it is solved and analyzed.

4. Results and Discussions

4.1 Electrical permittivity of PVDF

The complex electrical permittivity of PVDF material as explained is given by Drude theory from above mentioned equations considering: damping term given by log Γ= -16.41 and electrical permittivity (ξ_0) = 12 at low frequency and (ξ_{00}) = 4.5 at higher frequencies.

The following figures determine the imaginary and real plot of electrical permittivity of PVDF material in accordance with Drude theory.

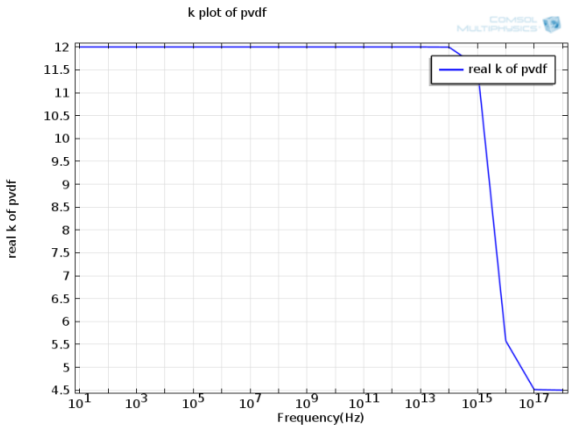

Fig.3a Real part of electrical permittivity of PVDF.

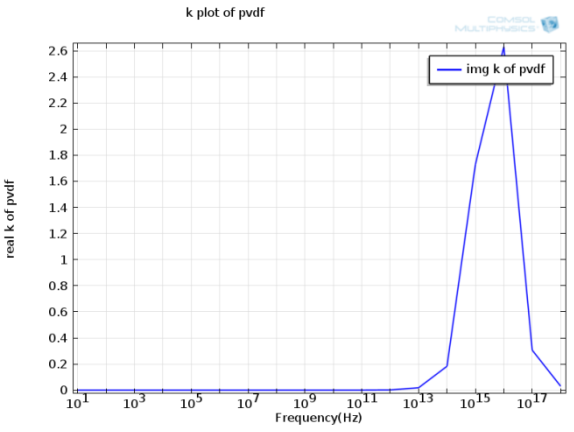

Fig.3b Imaginary part of electrical permittivity of PVDF.

4.2 3D Modeling

In order to determine the characteristics in 3D model, three geometries were drawn with loading fractions of 0.03, 0.12, 0.1575 corresponding to 4, 16, 21 spheres. The radii of the Al disks are considered to be 35nm and that of the shell to be around 45nm which are enclosed in a cube (polymer matrix) of side 800nm. When an alternating voltage of 1 volt is applied, an electric field is generated in the dielectric using the boundary conditions.

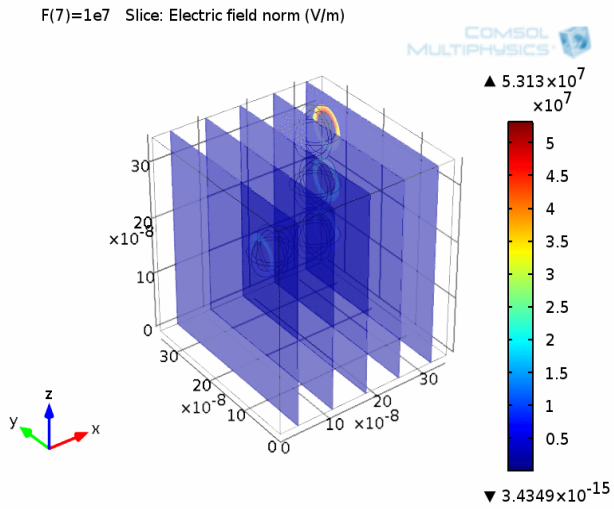

Fig.4a Electric field generated in nanodielectric with f = 0.03.

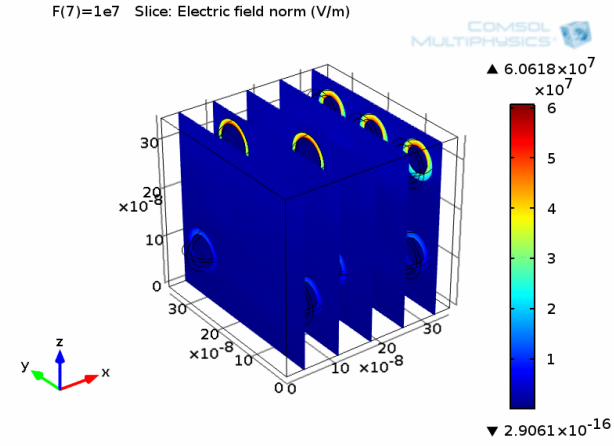

Fig.4b Electric field generated in nanodielectric with f = 0.12.

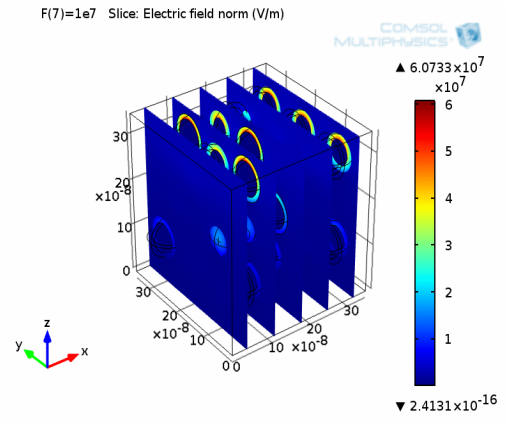

Fig.4c Electric field generated in nanodielectric with f = 0.1575

Figure (4) shows the slice plots of electric field Distribution in the 3D dielectrics with nanofillers of fraction: 0.03, 0.12, and 0.1575.

Highest enhancement of the electric field is observed in the samples with loadings values close to the percolation threshold. The net electrical field of the composite increases with loading and results in a high net polarization. The corresponding loading fraction is close to the percolation threshold $f_c = 0.16$.

In the presence of electric field, there are two polarizations acting on the medium. The first is the polarization of the PVDF matrix and the second one is the local polarization due to the Al fillers. These two polarizations contribute to the net effective polarization. With an increase in net polarization, there is also increase in electrical permittivity of the composite.

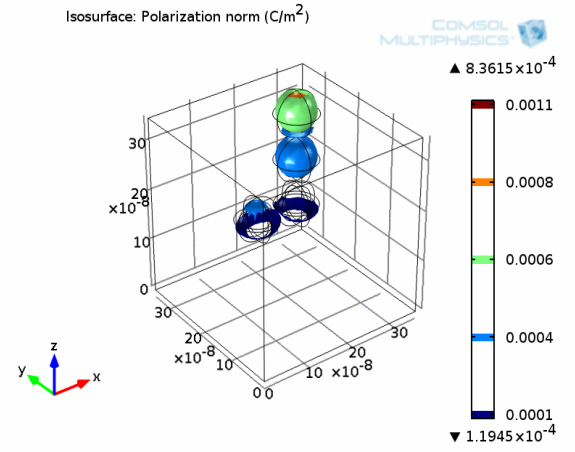

Fig.5a Real part of electrical permittivity of PVDF

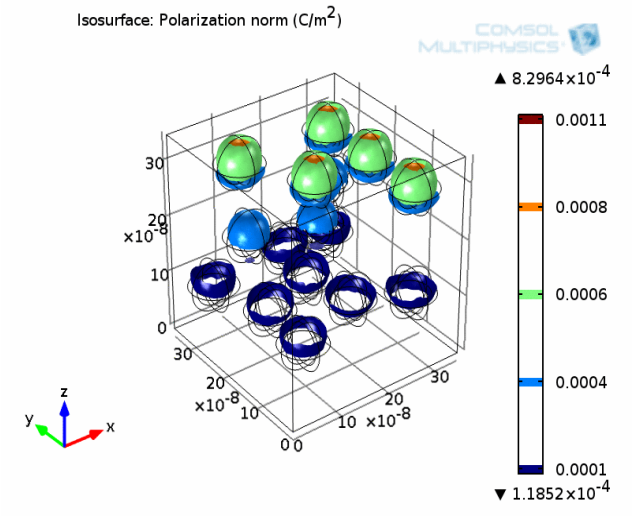

Fig.5b Polarization generated in nanodielectric with f = 0.12

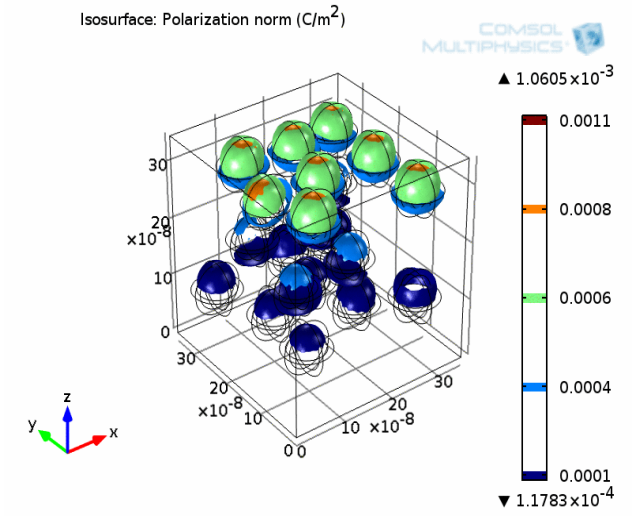

Fig. 5c Polarization generated in nanodielectric with f = 0.1575

4.4 K calculation using EMTs

The K value of the medium is calculated using the effective medium theory equations 9 and 10.
In Figures 6a & 6b, both Maxwell Garnett and Symmetric Bruggeman models gave an electrical permittivity of the composite in good agreement with the experimental values we obtained in a similar composite at the same loading. The effective electrical permittivity decreases at higher frequencies which is due to decay of ionic and polarization.

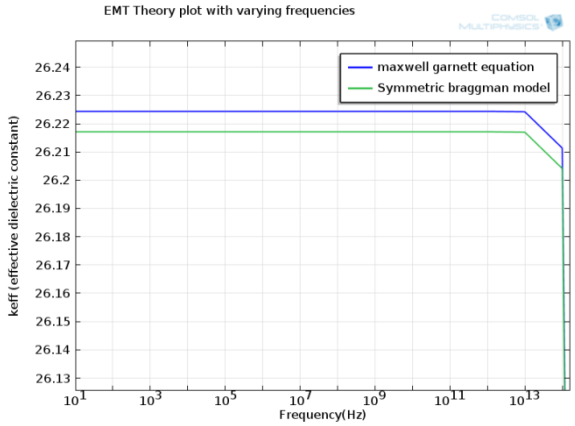

Fig.6a EMT plot of Maxwell Garnett and symmetric Bruggeman model at a loading f = 0.1575.

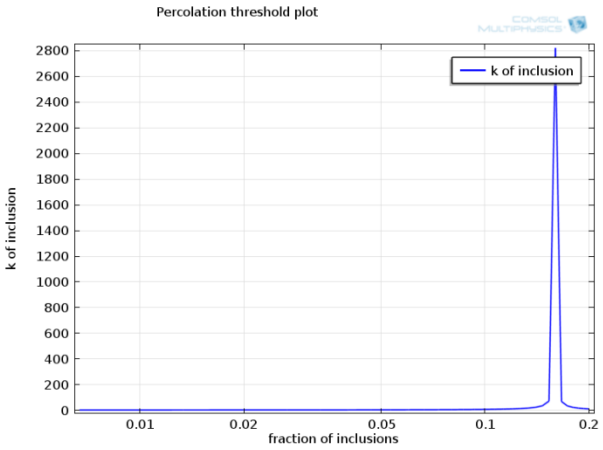

Fig.7 Plot between loading of nanofiller and electrical permittivity of the composite calculated using equation 12.

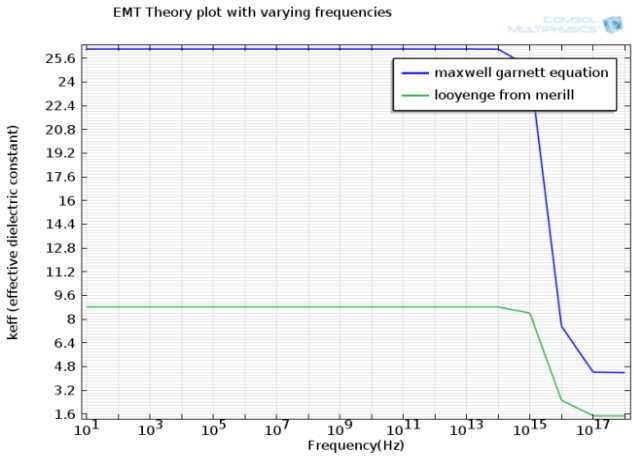

Fig. 6b EMT plot of Maxwell Garnett and Looyenga model at a loading f = 0.1575.

4.5 Percolation Threshold

The technique of preparing percolative composites to increase electrical permittivity (K) 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. Figure 7 shows an increase of permittivity from 12 of bare PVDF to 2800 of the nanocomposite at percolation threshold f = 0.16.

4.6 Case study at the interaction of two core-shells

We also investigated the close interaction of the core-shell nanoparticles dispersed in polymer and its effect on the net polarization. As expected with the use of a capping shell for electrical insulation of metal cores, the simulation results shown in Figure 8 indicate a drop in net polarization by a factor of 3 at the contact region.

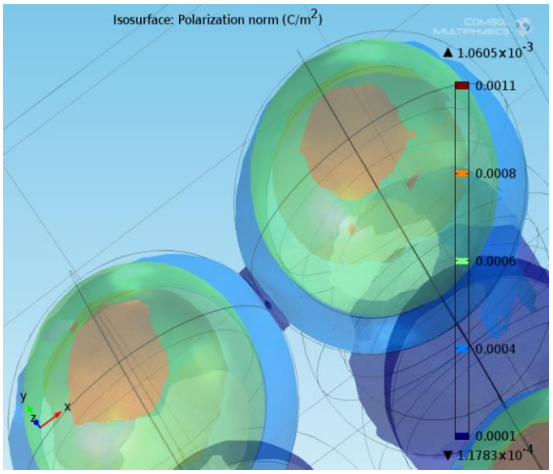

Fig.8 Demonstration of variation of polarization at the interaction of alumina shells.

5. Conclusion

Complex electrical permittivity of PVDF is calculated using Drude theory and that of aluminium 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 3D models, and graphs were plotted to explain the phenomenon of percolation. Significant increase in electrical permittivity of the composite (K = 2800) is achieved when compared to electrical permittivity of bare polymer (K = 12) by introducing 35nm sized Al nanoparticles. Effective electrical permittivity of the composite was also calculated using EMTs of Maxwell-Garnett, symmetric Bruggeman and looyean model. Like the percolation theory, EMTs also predict an increasing trend of electrical permittivity with an increase in volume fraction of the filler. Also variation of polarization near the shell interaction is studied and plotted.

6. Acknowledgments

This material is based upon work supported by the Texas State Fund to the University of Houston Center for Advanced Materials (CAM).

References:

1. "Effective Medium Theory of Nano dielectrics for embedded Energy Storage Capacitors, R. Bikky, N.Badi, A. Bensaoula", COMCOL Conference 2010 Boston, ISBN: 978-0-9825697-4-0, Newton, MA,October 7-9, 2010.
2. V. Myrochnychenko and C. Brosseau, "Finite-element method for calculation of the effective permittivity of random inhomogeneous media", Physical Review E 71, 016701, 2005.
3. P Debye " Polar Molecules" Chemical Catalogue Co NY (1929)
4. 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.
5. 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.
6. 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.
7. Lucia B Scaffardi and Jorge O Tocho, "Size dependence of refractive index of gold nanoparticles", Institute Of Physics Publishing, Nanotechnology, 17, 1309–1315, 2006.
8. Yang Shen et al, "High Dielectric Performance of Polymer Composite Films Induced by a Percolating Interparticle Barrier Layer", Adv. Mater. 2007, 19, 1418–1422.
9. C. W. Nan, Y. Shen and Jing Ma, "Physical properties of composites near percolation", Annu. Rev. Mater. Res. 2010. 40:3.1–3.21
10. Geoffrey Grimmett, "Percolation", Springer link, 1991.