Percolation, Electrical Conductivity, and EMI Shield Analysis of CNT Composites

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Won Sup Song

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Approved by:

Dr. Raghuram V. Pucha, Advisor
School of Mechanical Engineering
Georgia Institute of Technology

Dr. Satish Kumar, Second Reader
School of Materials Science and Engineering
Georgia Institute of Technology

Date Approved: [Date Approved by Committee]

TABLE OF CONTENTS

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Summary

Analysis of Carbon Nano-Tube (CNT) filled polymer composites is the focus of this work. CNT composites have far-reaching applications ranging from being applied in electronics as conductive polymer thin-films, in light weight aircraft structural components, and in many other engineering disciplines. These nano-composites are challenging to process and scalability and cost-effectiveness in manufacturing are yet to be achieved. Upfront models for electrical characterization of CNT composites are developed and analyzed for quick what-if analysis, and cost-effective solutions in manufacturing for various applications. Representative Volume Element (RVE) models with material homogenization conditions are developed in generating a 3D network of fillers within the RVE, which involve placing fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE is part of a larger network of RVEs. The RVE models with 3D network of CNTs within RVE developed are used for percolation, electrical conductivity and Electromagnetic interference (EMI) shield effectiveness (SE) of CNT-based polymer composites.

CHAPTER 1

INTRODUCTION

Carbon nanotube (CNT) reinforced polymer composites are finding increased interest due to their conductive properties in addition to their excellent mechanical properties. Many review articles [1] and research papers have been published in the last decade on CNT based polymer composites. Polymer / CNT composite films and fibers are also attractive in many potential applications such as sensors and electronics [2-4]. While significant insights have been achieved on various processing techniques in the manufacturing of CNT polymer composites, there are still many unresolved issues that need to be addressed theoretically and experimentally to harness the maximum benefit from these random heterogeneous materials.

The manufacture of nanofiller composites encounters many processing challenges. Even with the excellent properties reported in literature through controlled experiments [5], there exists a considerable gap between the individual properties of filler and their composite property [6]. The gap between predictions and experimental results [7] arises from imperfect dispersion and poor load transfer. For example in PNC, CNT agglomeration impacts the diameter and length distributions of the filler and overall is likely to decrease the aspect ratio. While significant insights have been achieved on various processing techniques, there are still many unresolved issues that need to be addressed theoretically and experimentally to harness the maximum benefit from composite systems with nanofillers. Design and analysis models with quick what-if analysis are needed to quantify the effects of various process parameters on the desired properties of composites with various nanofillers.

Computational modeling techniques for determining the mechanical and electrical properties of nanocomposites have proven to be very effective through parametric studies to facilitate the design and development of nanocomposites[8]. Molecular modeling is a powerful tool for studying atomic interactions at the nanometer length scale. Due to the discrete nature of these techniques, they are often limited by the length and time scales that can be achieved in the simulations, and thus these techniques can be computationally prohibitive [9]. The applicability of continuum mechanics to nanocomposites is debatable [10]. Even though continuum theory loses direct applicability at the atomic scale, many works directly applying continuum mechanics to nanostructures and nanomaterials have reported meaningful results and have helped elucidate many issues[11, 12]. Finite Element Analysis (FEA) can be used for numerical computation of bulk properties based on the geometry, properties and volume fraction of constituent phases [13]. Representative Volume Element (RVE) based approaches are also popular in evaluating the effective material properties of randomly distributed short fiber composites [14, 15]. FEA-based approaches with unit-cell [16] and multi-cell RVEs [17, 18] had been used to investigate the effect of CNT aspect ratio on the load transfer between CNT and matrix.

Conductive CNT/polymer composites can be applied to several fields, such as highly sensitive strain sensors, medical devices, portable electronics devices, etc. The electrical properties of these composites result from what is known as the percolation threshold[19], that is, the volume fraction of conductive filler within the polymer at which the composite electrical conductivity spikes. There are many different methods for electrically analyzing a CNT polymer nanocomposite. Among the various methods Resistor-Capacitor (R-C) network models [20] "replace" contacting CNTs with equivalent resistors and non-contacting CNTs with equivalent capacitors. In this approach, an equivalent circuit is constructed by combining these equivalent resistors and capacitors in series and parallel based on how they relate to one another geometrically by contact within chains and the relationships between non-contacting chains of CNTs within the composite. Furthermore, another factor that may affect the electrical conductivity is tunneling current present among CNTs that are very close, but not touching, and it may be useful to quantify these effects on the overall electrical conductivity within the equivalent circuit. Once voltage is applied from one face of the composite within the model to another face, the current flowing through the composite can be determined numerically and the electrical conductivity can be calculated.

Many electrical conductivity models are proposed in the literature [21] based on various factors to predict the conductivity behavior of PNCs in order to achieve more efficient composite design that could result in desirable conductive PNCs. As these models based on theoretical and empirical equations are tuned to reproduce available experimental data they are applicable only near the critical transition point where the composite system moves from a perfect insulator to conductor, and when the matrix phase is a perfect insulator. Many researchers have studied simulation based approaches with electrical networks of fillers to predict the percolation and conductivity of composites with conductive fillers [22].

Though limited literature is available [23, 24] computational methods like finite element approach can predict electrical conductivity and percolation threshold of PNCs for various constituent morphology and properties. Monte Carlo methods are a broad class of computational algorithms that rely on repeated random sampling to obtain numerical solutions. Efficient percolation algorithms integrated with Monte Carlo methods are needed for developing RVE based design and analysis tools for electrical conductivity of nanocomposites.

An electronic device is considered electromagnetically compatible with its surrounding if it does not interfere with other devices or itself, and it does not affected by emissions from other devices [25]. Conventional conductive polymer composites made of stainless steel fibers, nickel coated carbon fibers are cost prohibitive for EMI applications because of the high concentration of filler required to achieve an adequate level of shielding. At the same filler loading, polymer filled with nano-sized carbon filler has higher EMI Shielding Effectiveness (SE) than polymer filled with micro-sized carbon filler. The EMI SE of a material is defined as the ratio of transmitted power to the incident power. The distance required by the power wave to be attenuated to 37% is defined as the skin depth. A good material for EMI shield should have high conductivity and high permeability along with a sufficient thickness to achieve the required number of skin depths.

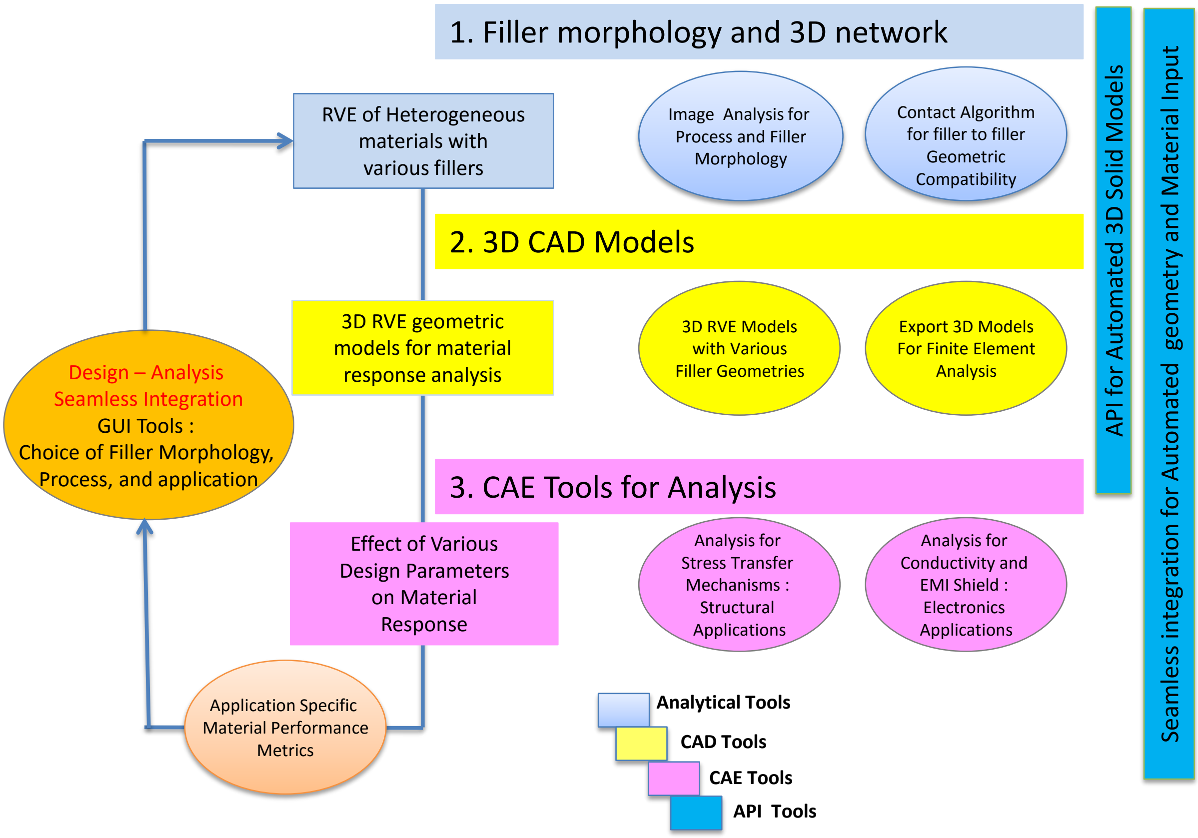


Figure 1: Seamlessly Integrated CAD/CAE Approach

Research Objectives:

(1) Develop RVE models with 3D network of fillers within the RVE using seamlessly integrated CAD/CAE approach. Both probability distribution functions and random functions of process variables are used to develop the RVE models.

(2) Develop algorithms for different boundary conditions within a homogenized RVE.

(3)Develop 3D models with and without homogenized boundary conditions for subsequent percolation, electrical conductivity and EMI shield Analysis to quantify the effect of these boundary conditions of effective properties.

CHAPTER 2

HOMOGENIZED RVE MODELS

1. 3D RVE models: Considerable work has already been done in the research group in developing algorithms for seamless integration of analytical and CAD tools for developing 3D RVE models for various composites with 3D network of fillers within RVE (see Figure 1). Fillers, such as carbon nanotubes, silicon carbide nanoparticles, exfoliated graphite nano-platelets, soft tissue, composite fibers and syntactic foams (see Figure 2) are automatically generated and a 3D network of fillers within RVE are arrived using seamless integration of analytical, 3D solid modeling and Finite Element Analysis tools. The 3D network of fillers within RVE is controlled using a uniform grid, close packing algorithm, random distribution or by various probability distribution functions that control filler parameters like diameter, length, etc. These parameters are quantified using image analysis or through analysis of experimental composites from the literature. The primary objective of this research is to seamlessly generate 3D RVE models with filler geometries and viable FEA models of various composite systems based on user input that replicate and predict properties of experimental composites. My work is primarily focused on RVE models for CNT composite models for electrical conductivity applications.

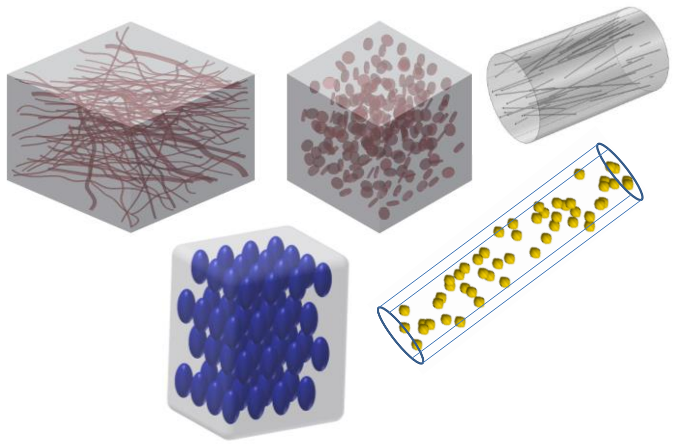


Figure 2. 3D RVE models for various composite applications

2. Algorithms for different material boundary conditions and homogenized RVE:

RVE models with material periodic conditions are developed in generating a 3D network of fillers within the RVE. Computational homogenization in 3D RVE models is achieved using two approaches. In the first approach, statistical analysis with number of realizations is performed with increasing RVE size of randomly generated CNT within polymer. In statistical analysis, the filler that exceeds the RVE are translated until they find new spatial location within RVE. Simulations with increasing RVE size are performed until the standard deviation of computed apparent property for each RVE size is minimum to predict the critical RVE size. In the second approach, RVE models with material periodic boundary conditions are developed, which involve placing fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE is part of a larger network of RVEs. Percolation threshold analysis of CNT filled polymer composites is presented using both computational homogenization approaches. It is demonstrated that computational homogenized models with material periodic conditions are independent of RVE size and provide homogenized results and are computationally efficient compared to statistical models.

Homogenization techniques allow heterogeneous materials such as composites, to be treated by continuum models, thus simplifying the computational analysis of these materials. Homogenization methods have extensively been used to estimate effective properties of random heterogeneous materials from the knowledge of the constitutive laws and spatial distribution of the constituents [26]. In homogenization methods the proposed estimations are given for random composite media with an infinite extension, and can therefore be denoted as asymptotic estimates [27]. Computational homogenization methods use numerical techniques and simulations on samples of the microstructure. In these models the notion of representative volume element (RVE) is of paramount importance [28]. There are many definitions for RVE in literature [29]. The RVE is the smallest volume over which a measurement can be made that yields a property value representative of the whole [26]. In continuum mechanics for a heterogeneous material, RVE can be considered as a volume that represents a composite statistically, which is small enough to be considered for macroscopic property representation and sufficiently large to ensure the independence of boundary conditions [30]. The overall properties of a sufficiently large domain in a random medium are deterministic and is independent of the type of boundary conditions, which requires a rather large size of RVE [31]. This rigorously justifies the fact that one can numerically compute the homogenized properties by simulating a single realization of a large heterogeneous medium. For volumes smaller than the RVE, a representative property cannot be defined and the continuum description of the material involves statistical volume element (SVE) and random fields.

Limited quantitative knowledge is available about critical RVE sizes of various engineering materials relating the size of RVE of the heterogeneous material to the characteristics length of inclusions [29]. For example in the case of reinforced elastic composites, the minimum proposed 2D RVE size is equal to twice the reinforcement diameter[32]. Numerical techniques can be used to compute the homogenized properties by the simulation of one single realization of the large medium and also in determining a critical size of RVE. For example Monte-Carlo simulations [33] were used to predict RVE size of disordered distributions of spheres in a matrix.

Statistical RVE models with spatially distributed 3D network of filler material represent an idealization of the actual structure of CNT polymer composite. In our previous work, statistical RVE based 3D models [34] with quick what-if analysis were presented to quantify the effects of various process parameters on the desired properties of CNT polymer composites. In these models the choice of statistical RVE is usually not unique, but it should be large enough to represent the filler morphology and spatial distribution and as small as possible to reduce the computation cost. Determining a critical size of such statistical RVE [34], which can predict a homogenized property of interest, is computationally very expensive. Computational homogenization [35, 36] with material periodic boundary conditions is one alternative to reduce the computational complexity. In computational homogenization approaches, material periodic boundary conditions are applied to the RVE, which involve placing fillers that exceed the RVE into their respective position as if the RVE is part of a larger network of RVEs. The property of interest may include mechanical properties such as elastic moduli, percolation threshold, electrical and thermal properties, and other averaged quantities that are used to describe physical systems.

In this work, RVE models with a 3D network of fillers within the RVE are developed with algorithms for various boundary wall conditions. Computational homogenization in 3D RVE models is achieved using two approaches. In the first approach, statistical analysis with number of realizations is performed with increasing RVE size of randomly generated CNT within polymer. In statistical analysis, the filler that exceeds the RVE are translated until they find new spatial location within RVE. Simulations with increasing RVE size are performed until the standard deviation of computed property is minimum to predict the critical RVE size. In the second approach, RVE models with material periodic boundary conditions are developed, which involve placing fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE is part of a larger network of RVEs. The following sections describe the development of RVE models with various boundary wall conditions and material periodicity. A computational methodology with seamless integration of analytical and CAD tools [34] is adopted to develop statistical analysis models of varying RVE size with translate boundary conditions. An efficient percolation threshold algorithm is developed to monitor filler-to-filler shortest distance in predicting the percolated network within RVE is presented in Chapter 3. . Percolation threshold analysis of CNT filled polymer composites is also presented in chapter 3 using both computational homogenization approaches.

Boundary conditions are needed to homogenize the 3D RVE model for various applications. Three types of boundary conditions namely translate, cut-off and periodic boundary conditions are considered in this work.

1. The translate boundary condition involves moving the CNTs that exceed the RVE until they find a new location based on filler-to-filler contact algorithm.
2. The cut-off boundary condition involves locally trimming the exceeding CNTs around the limits of the RVE.
3. The periodic boundary condition involves placing CNTs that exceed the RVE into their respective position on the opposite face of RVE as if the RVE were part of a larger set of RVEs.

In all cases the CNT are added until the desired volume fraction is reached for subsequent analysis. In the 3D analysis for mechanical or electrical analysis any combination of these conditions can be used as appropriate.

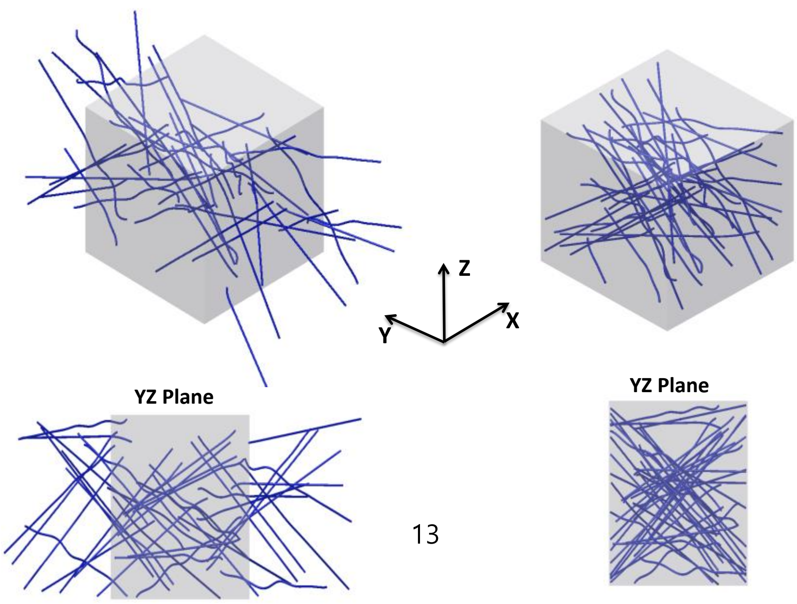


Figure 3: 1-3-3 Boundary Conditions case
(Translate in X , Periodic in Y and Z)

For example, if the 3D RVE models are used for predicting the effective tensile modulus of CNT composite, the 2D faces in the loading direction are subjected to translate boundary conditions and the CNTs are relocated inside the RVE in the X direction and periodic boundary conditions are applied in other to faces, Y and Z. This condition is denoted as 1-3-3 shown in Figure 3.

If the 3D RVE models are used for predicting effective electrical conductivity of CNT composite using Finite Element Analysis, the 2D faces in X direction, where the voltage is applied are subjected cut-off boundary conditions and periodic boundary conditions are applied in other to faces Y and Z. This condition is denoted as 2-3-3 shown in Figure 4.

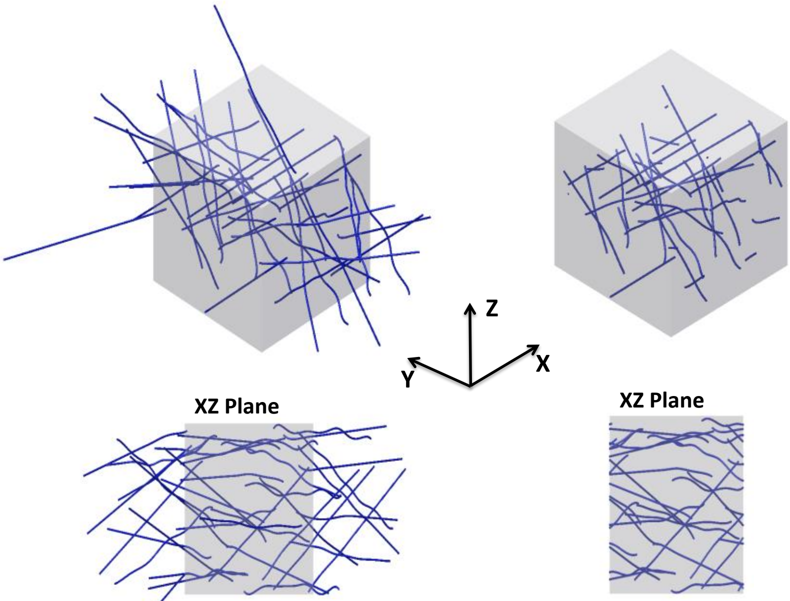


Figure 4: 2-3-3 Boundary Conditions case (Cut-off in X , Periodic in Y and Z)

If the RVE models are used for quantifying the electrical conductivity of composite

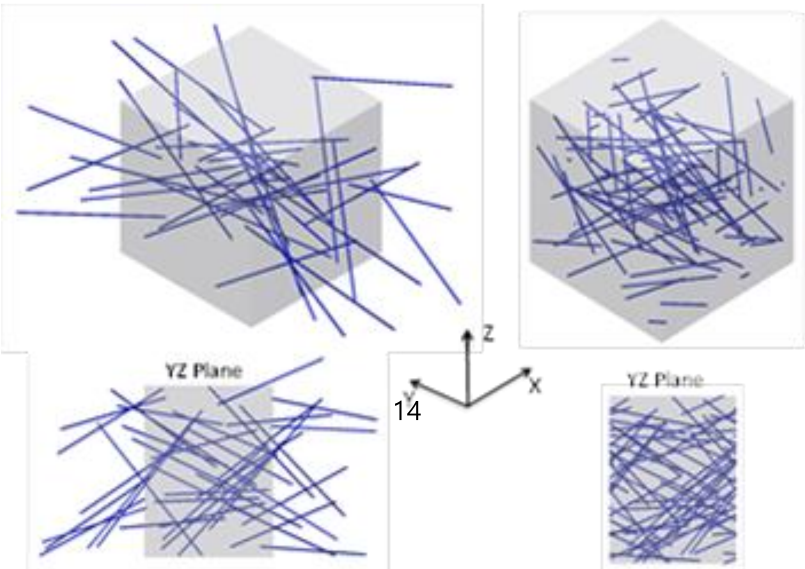


Figure 5: 3-3-3 Boundary Conditions case (Periodic in X,Y and Z)

system using Resistor – Capacitor (R-C) approach [20] periodic boundary conditions are applied on all three faces of RVE. This condition is denoted as 3-3-3 shown in Figure 5.

To develop a robust algorithm for periodic boundary conditions many cases of CNT crossing the RVE faces have to be considered. Figure 6 shows example of some of the cases

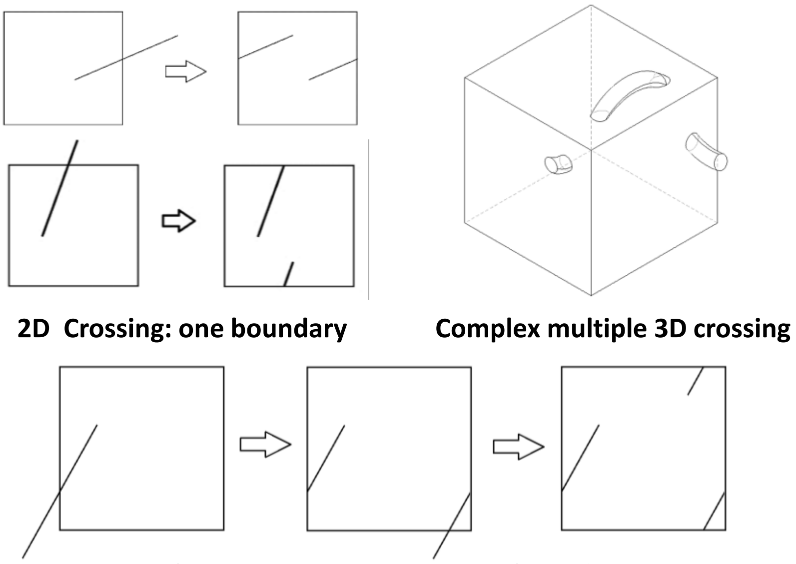


Figure 6: Example boundary conditions cases

considered and Figure 7 illustrates the steps involved in the algorithm application of periodic boundary conditions. The CNTs are generated within the RVE using a spline function defined

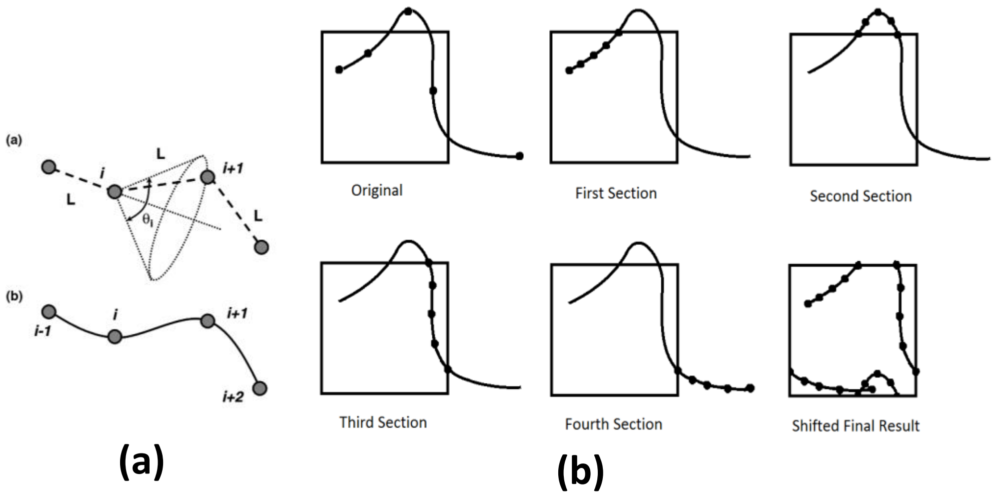


Figure 7: (a) Filler Generation and (b) procedure for applying Periodic boundary conditions

by number of segments. As shown in Figure 7(a), the first point of the spline is located randomly within RVE and subsequent segment points are generated by the maximum angle defining the waviness of CNT. If the original CNT spline is defined by five segments, as shown in Figure 7(b), each portion of CNT crossing the RVE boundary are redefined using five segment points when periodic boundary conditions are applied. As shown in figure 7(b), at the end of boundary conditions process, each portion crossing the RVE boundaries is shifted to other faces of RVE maintaining the filler morphology and periodicity. Figure 8 illustrates material periodic boundary conditions, which involves placing the fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE with 3-3-3 boundary conditions were part of a larger set of RVEs.

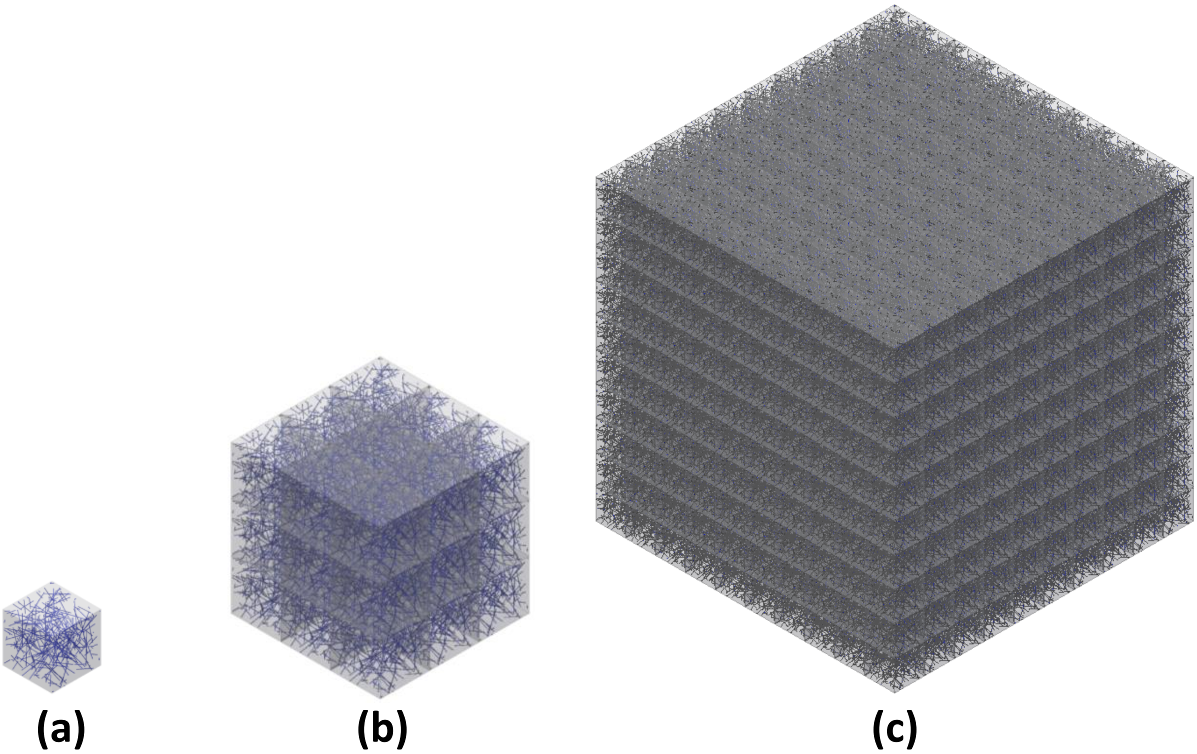


Figure 8: Illustration of Large RVE sample with periodically repeated RVEs. (a) RVE: 3000 x 3000 x 3000 nm (b) 9000 x 9000 x 9000 nm (c) 30 x 30 x 30 μ

RVE models with random distribution of CNT within polymer are developed for statistical analysis. In all statistical analysis models, translate boundary wall conditions are used by moving the fillers that exceed the RVE until they find a new spatial locations within RVE as shown in Figure 9. To predict the critical RVE size, models with increased RVE sizes are developed as shown in Figure 10. Figure 11 shows models with increased volume fraction for each RVE size.

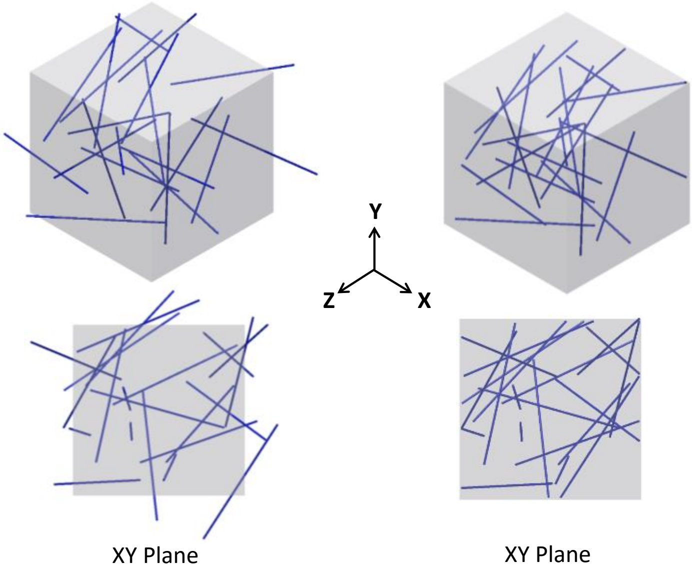


Figure 9: 1-1-1 Boundary condition - Translate in X, Y and Z, RVE 2000 x 2000 x 2000 nm, Volume Fraction: 0.2%

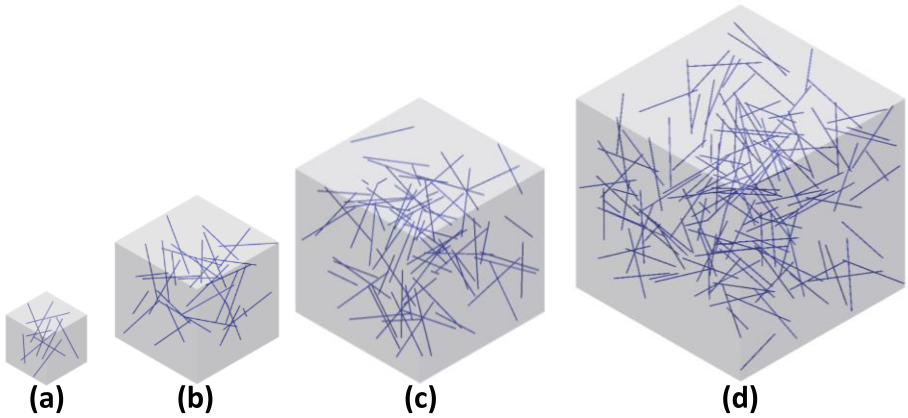


Figure 10: RVE Models for Statistical Analysis - (a) RVE: 2000 x 2000 x 2000 nm (b) 3000 x 3000 x 3000 nm (c) 4000 x 4000 x 4000 nm (d) 5000 x 5000 x 5000 nm , Volume fraction: 0.1%

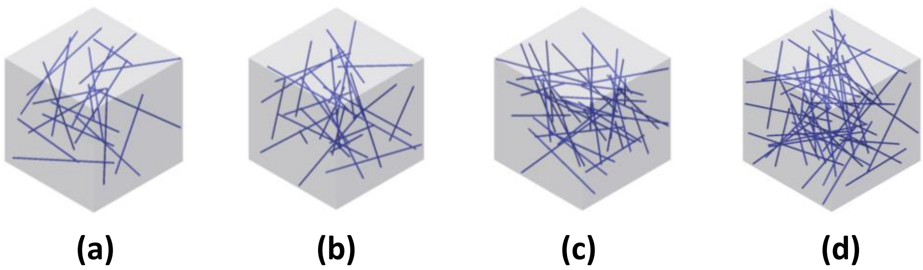


Figure 11: RVE Models for Statistical Analysis - (a) Volume fraction : 0.2% (b) Volume fraction : 0.3% (c) Volume fraction : 0.4% (d) Volume fraction : 0.5%, RVE: 2000 x 2000 x2000 nm

CHAPTER 3

PERCOLATION ANALYSIS

3.1 Percolation Analysis in CNT Polymer Composites:

Experimental findings in CNT reinforced polymeric matrix materials have shown that conductivity follows a percolation like behavior [19]. The electrical conductivity of a composite is generally characterized by its dependence on the filler volume fraction. At low filler loadings, the conductivity of the composite is still very close to that of the pure polymer matrix. At some critical loading, called the percolation threshold, the conductivity increases several orders of magnitude with very little increase in the filler amount. Many theoretical [37] and simulation models [38] based on filler volume fraction are proposed in the literature to predict the percolation threshold and conductivity behavior of composites. Percolation analysis of CNT/polymer composites is considered in this work to demonstrate the developed computational homogenization models. Both statistical analysis models with translate boundary conditions (1-1-1) and homogenization models with material periodic boundary conditions (2-3-3) are used to predict the percolation threshold. A percolation threshold algorithm with boundary wall conditions is developed to monitor the shortest distance between added fillers in predicting the volume fraction at which a 3D network of percolated network is formed within RVE.

3.2 Statistical Analysis and critical RVE size:

Simulations for percolation analysis are conducted for various RVE sizes. As mentioned earlier, the RVE size is usually not unique, but it should be large enough to represent the filler morphology and spatial distribution to predict a homogenized apparent property of interest. For each RVE size CNTs are randomly added to polymer block. Translate boundary conditions (1-1-1, see Figure 9) are used by moving the CNTs that exceed the RVE until they find a new spatial location within RVE. A percolation threshold algorithm (see Figure 12) is used to track the CNTs, whose center-to-center distance is equal to the diameter of the CNT. Figure 13 shows the 3D network evolution during a typical statistical analysis for a specific RVE size. Percolation in X direction is defined when a conductivity path is achieved with connecting CNTs in the XY plane as shown in Figure 13 with bold CNTs. The volume fraction at which percolation happens is defined as percolation threshold. Because of the repeated random sampling of fillers within RVE used in the percolation analysis, the percolation threshold obtained varies when the analysis is repeated for the same RVE size as shown in Figure 14.

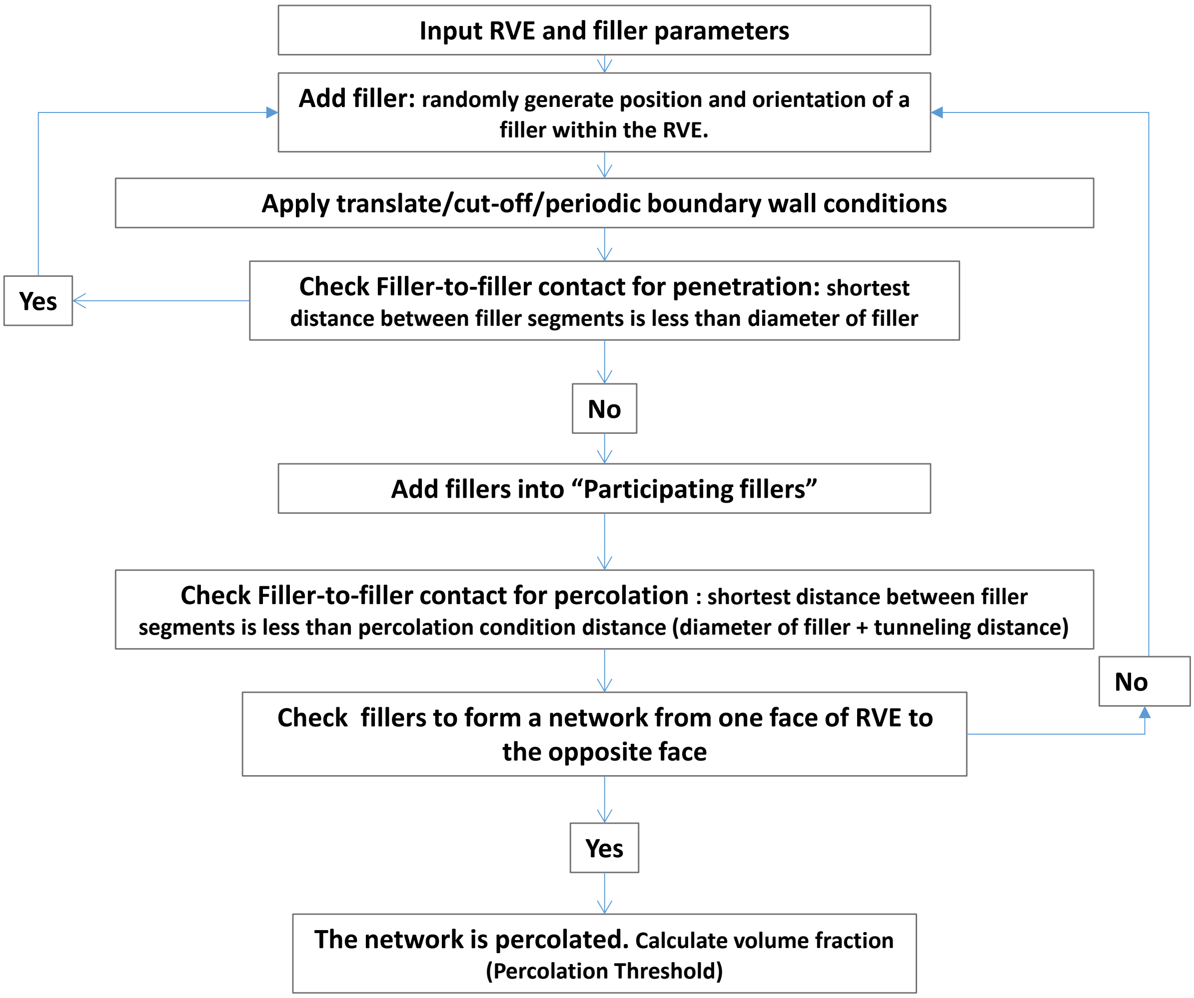


Figure 12: Percolation threshold algorithm with boundary conditions

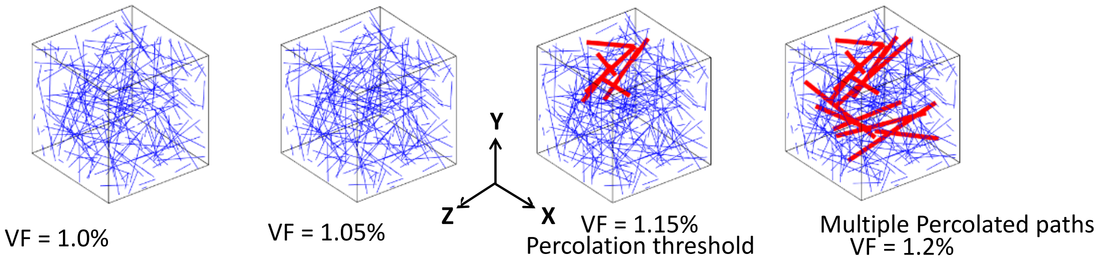


Figure 13: Statistical analysis illustration of 3D Network evolution for percolation and multiple percolated paths

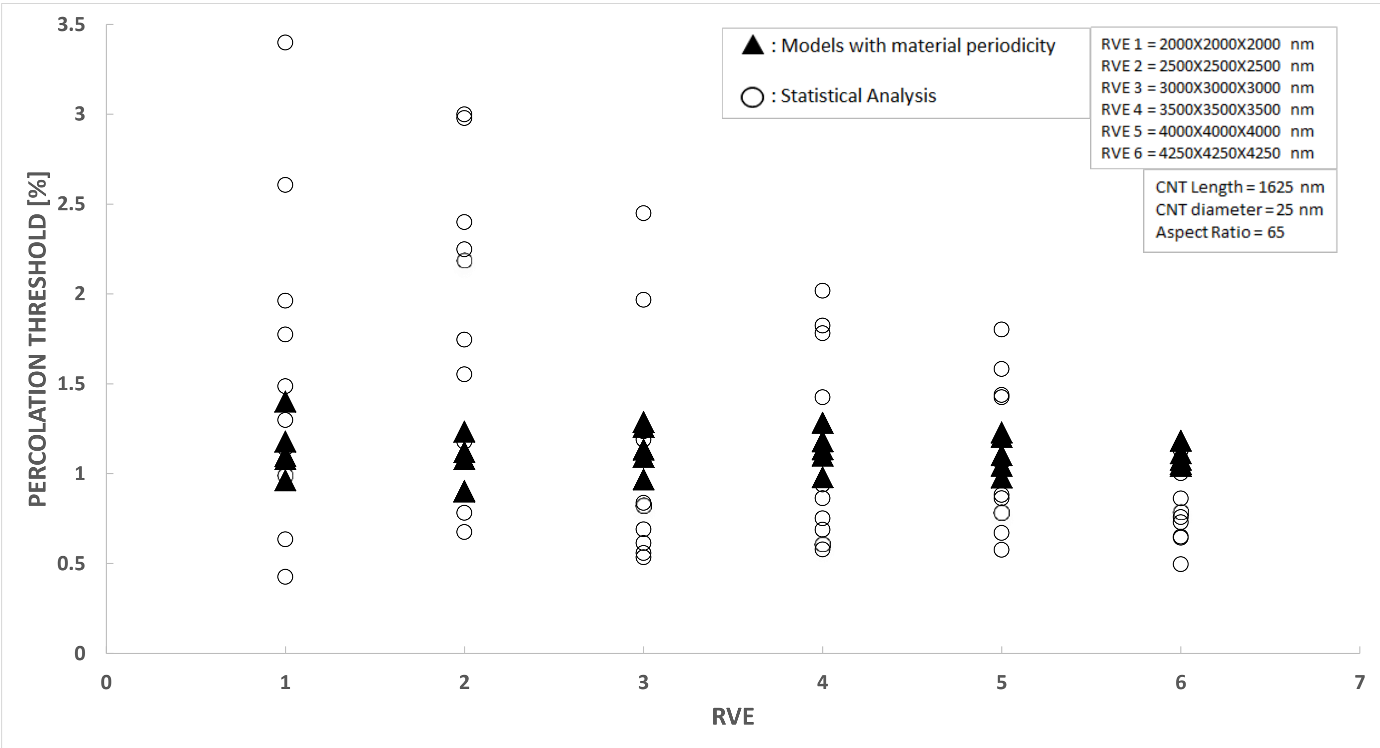


Figure 14: Percolation threshold results comparison and critical RVE size for statistical analysis

Percolation analysis for each RVE size is conducted for ten realizations and the percolation threshold values are plotted for each RVE size as shown in Figure 14 represented by unfilled circles. When the cubic RVE size is increased the statistical variation in the predicted percolation threshold values (unfilled circles) reduced as shown in the Figure 14. For a critical cubic RVE size of 4250 nm the standard deviation of percolation threshold values for ten realizations is less than 0.1, which is considered as a homogenized result.

Figure 15 shows comparison of percolation threshold values for various CNT aspect ratios. Predicted critical RVE size of 4250 nm with varying aspect ratio of CNT is used for this purpose. The percolation threshold values averaged over ten simulations match very well with the values reported in the literature [39] .

3.3 Computational homogenization models with material periodicity:

The percolation analysis using statistical models with translation boundary conditions (1-1-1) presented in the previous section indicates that the predicted percolation threshold values are dependent on RVE size. The percolation threshold values predicted exhibit statistical variation and are more scattered when the analysis is repeated for the same RVE size. For larger RVE sizes the scatter in the predicted percolation threshold gradually reduced leading to more homogenized results as shown in Figure 14. It is also important to note that percolation analysis with statistical models requires large RVE size to arrive at more homogenized results and are thus computationally expensive. Percolation analysis is also performed using computational homogenization models with material periodic boundary conditions to study the effect of boundary conditions and RVE size. 2-3-3 material periodic boundary conditions (see Figure 4) are used and the analysis is repeated for each RVE studied.

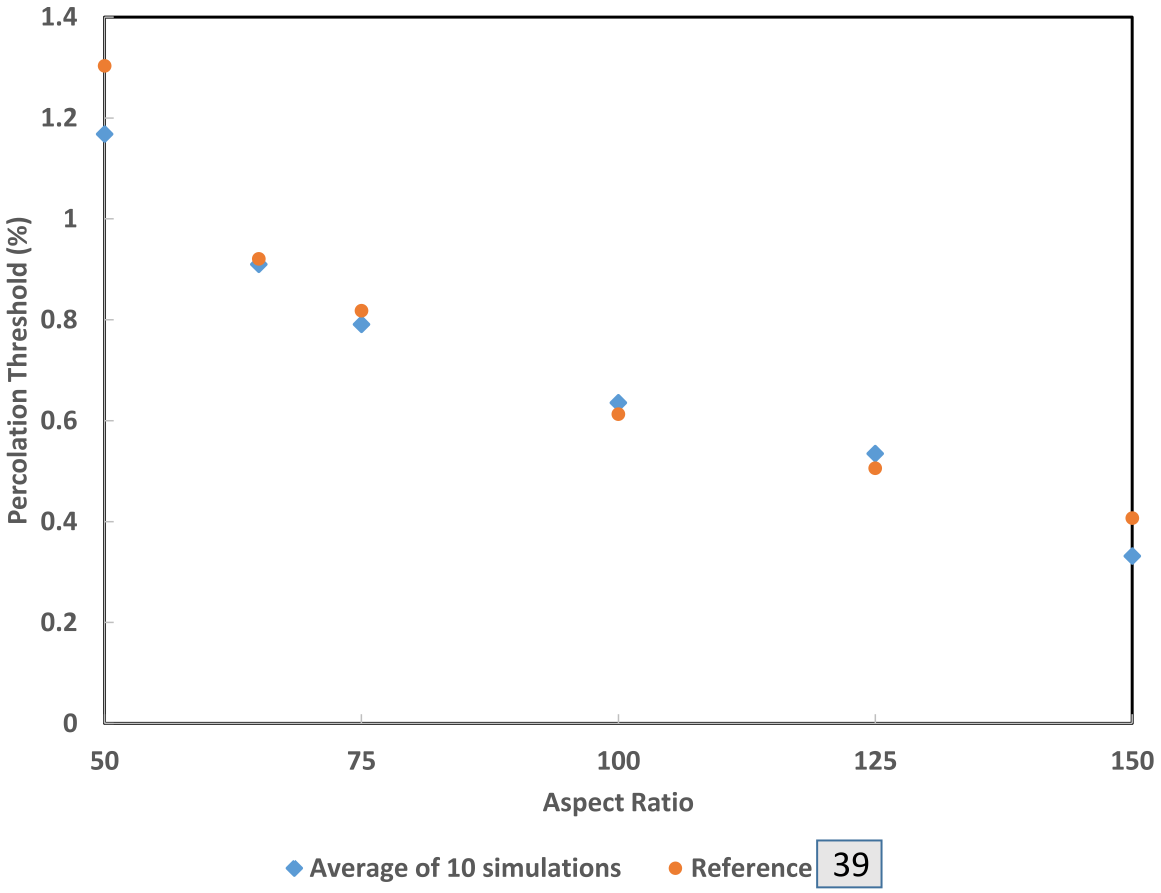


Figure 15: Validation of Percolation Analysis : Effect of Aspect Ratio

Figure 14 shows percolation threshold values predicted with material periodic conditions (filled triangles) for each RVE size. As shown in Figure 14, the statistical variation and scatter in percolation threshold values is low for models with material periodicity compared to statistical analysis models. Therefore only five simulations are performed for each RVE size. It is also noted from Figure 14 that the percolation threshold values predicted by models with material periodic conditions (filled triangles) are essentially independent of RVE size indicating that the results are homogeneous and can be obtained with less computational effort and smaller RVE size.

Figure 16 shows percolation threshold values for models with material periodicity for various RVE sizes. As can be seen from Figure 16, a homogenized value of percolation threshold is achieved independent of RVE size. Figure 17 shows standard deviation of percolation threshold values for various realizations using models with material periodicity which are consistently low for all RVE sizes studied.

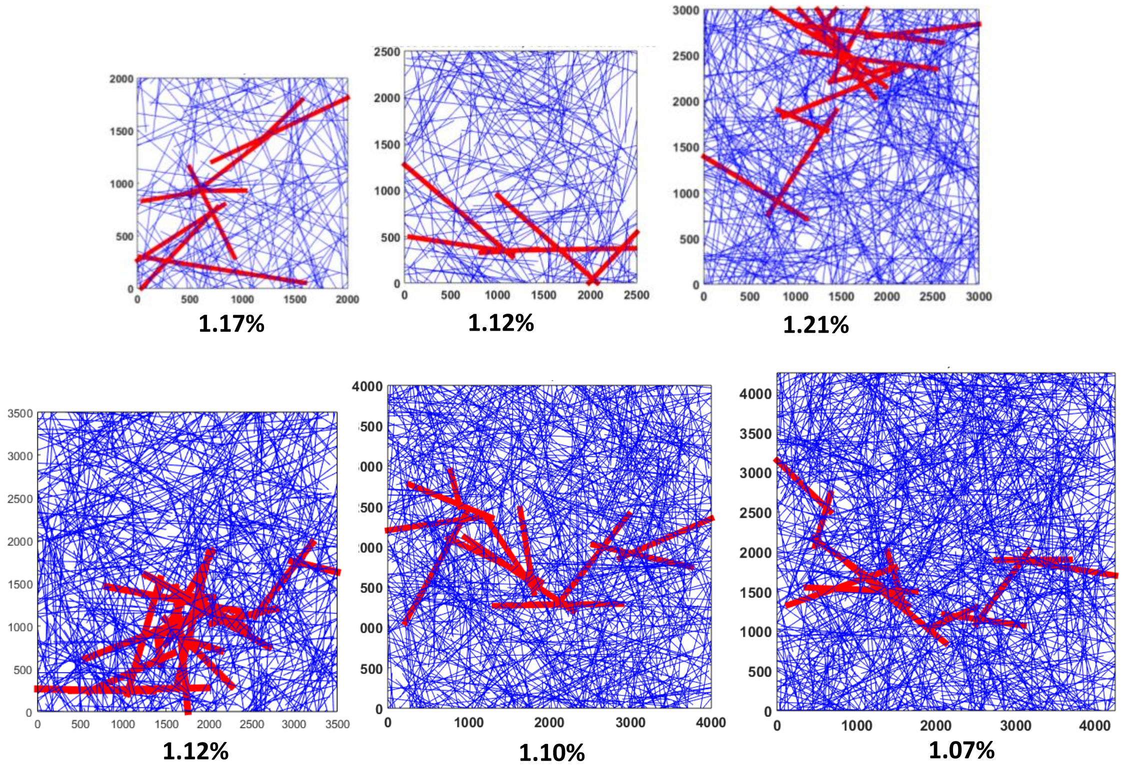


Figure 16: Percolation threshold values for models with material periodicity

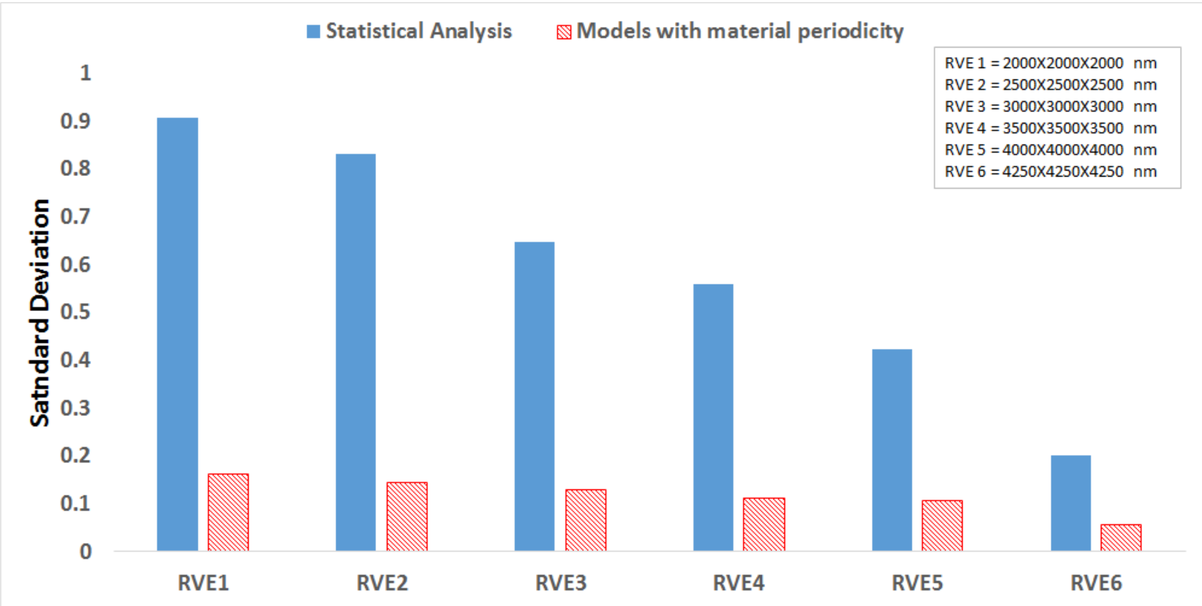
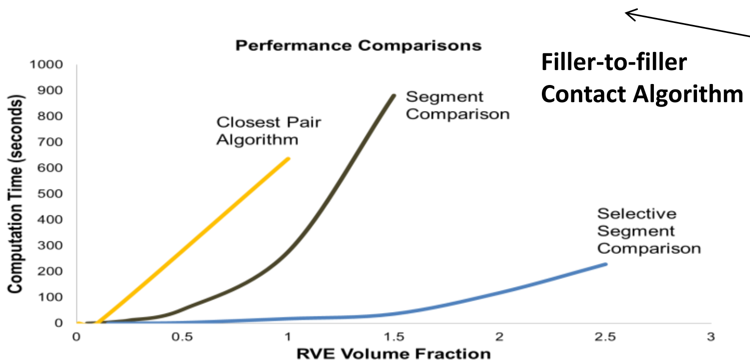


Figure 17: Standard deviation of percolation threshold values for various realizations

The standard deviation of percolation threshold values with statistical analysis on the other hand is very high for smaller RVE size and gradually reduces towards a homogenized solution for a large critical RVE size.

3D network modeling of nanocomposites requires that the distance between each filler be calculated to prevent unphysical inter-penetration of fillers. Algorithms for filler-filler contact are being developed in our research group and are demonstrated for high aspect ratio fiber nanocomposites. These algorithms are used to generate models without inter-filler penetration, check the spatial distribution among fibers in the model, and determine when the percolation is achieved in the 3D system.

Process	Elapsed Time (seconds x 10^{-5})
Declaring All Variables	2
Determine Length	15.7
Determine Diameter	5 – 16
Create CNT Geometry	241 – 3000
Check Contact	≈30,000+



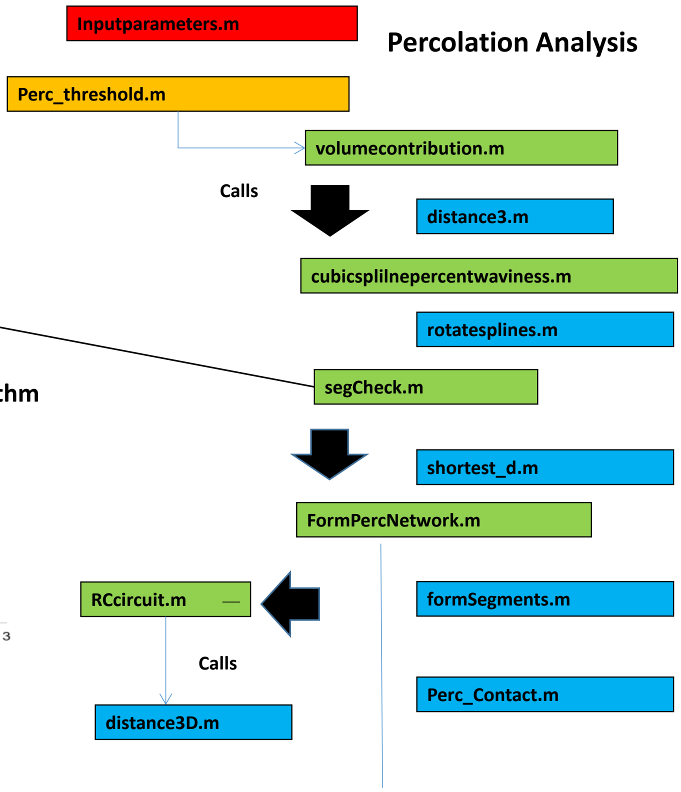


Figure18: Computational time and Efficiency of filler-to-filler contact algorithm in percolation analysis

In the percolation analysis the computation time increases with volume fraction. The most computationally intensive part of the current code is the contact algorithm. Selective segment comparison method is 15 times faster than approach 2 at 1% volume fraction and nearly 100 times faster than approach 1 at 1% (see Figure 18). Though the selective segment comparison method has better running times, at higher volume fractions it still requires much time to run. To speedup of the algorithm, parallelization of the code is needed. By splitting the work among processors, the calculation of the distance can be done at the same time rather than serially. The current algorithm will be augmented with periodic boundary conditions for percolation analysis. For large RVE sizes with higher volume fraction of the filler High Performance Computing (HPC) facilities at Georgia Tech are used for reducing the computational burden.

Because of the repeated random sampling of fillers within RVE used in the percolation analysis – the percolation threshold obtained varies when the analysis is repeated. When the RVE size is increased the analysis tends to converge (see Figure 14). Using HPC determine the largest RVE size that results in homogenized solution with less variation in percolation threshold values. This work is currently in progress. Once homogenized solution with largest RVE size is found, the effect of filler aspect ratio and waviness on the percolation threshold will be quantified.

3.4 Implementation of Graph Theory:

Alternative approach to perform percolation analysis is to implement graph theory algorithm. CNTs are represented as nodes in the graph settings, and their contacts with other CNTs are mapped to give a graph characteristics. Using this algorithm, CNT networks with a higher volume fraction can be reached fast. The advantage of implementing graph theory algorithm is that it can profile multiple connections formed within local CNTs. Figure 19 shows each CNT represented as a node and connections each CNT has with other CNTs. Once relationships among CNTs are established, each pair, storing the location of contact point among CNTs, is once again defined as nodes and the distance among the contact points are mapped as shown in Figure 20.

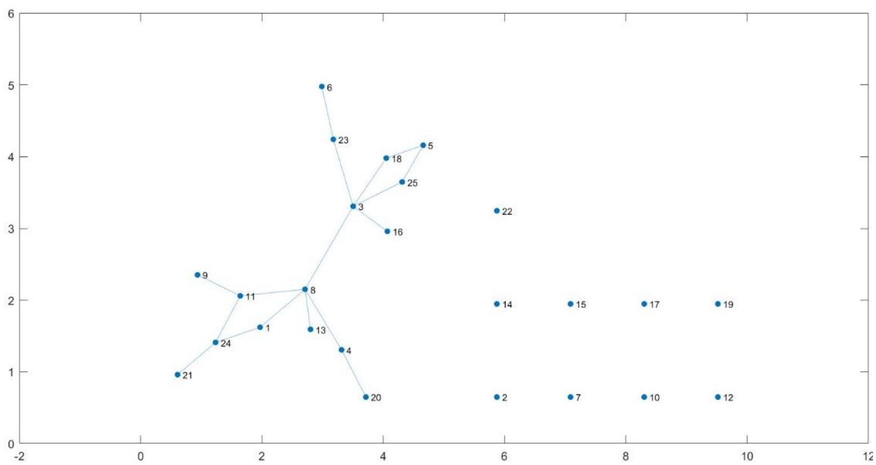


Figure 19. Graph of CNT Connections with Multiple Paths

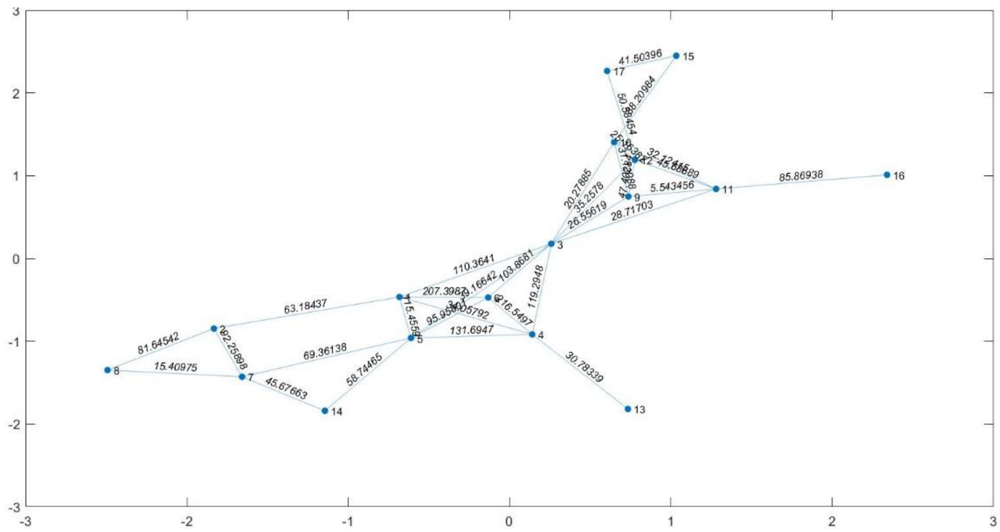


Figure 20: Circuit Representation of Graph in Figure 19

Figure 20 is also graphically represented in Figure 21. The complex relationships among CNTs are much more efficiently stored and analyzed in graph settings.

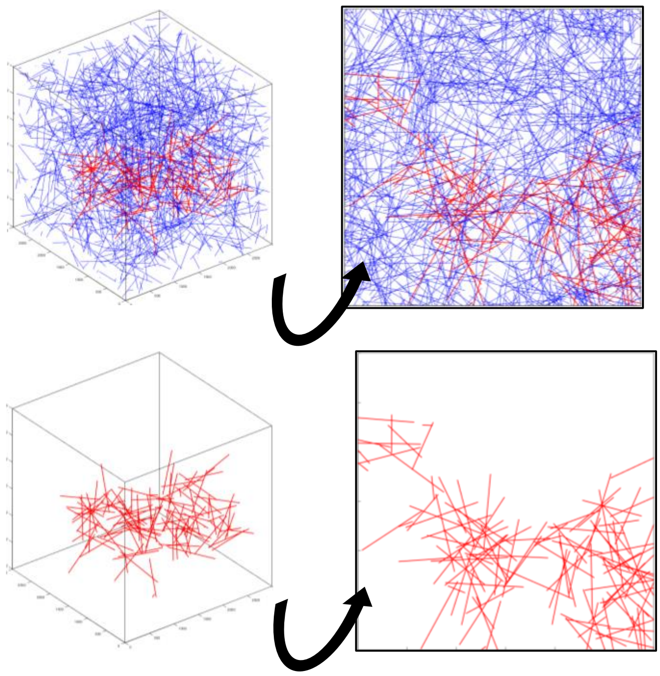


Figure 21: Graph Representation Result

CHAPTER 4

ELECTRICAL CONDUCTIVITY AND EMI SHIELD ANALYSIS

Carbon nanotube (CNT) reinforced polymer nano-composites (PNC) are finding increased applications due to their conductive properties in addition to their mechanical properties. Polymer / CNT composite films and fibers are also attractive in many potential applications such as sensors and electronics [40]. The electrical conductivity of a composite is generally characterized by its dependence on the filler volume fraction. At low filler loadings, the conductivity of the composite is still very close to that of the pure polymer matrix. At some critical loading, called the percolation threshold, the conductivity increases several orders of magnitude with very little increase in the filler amount. After this region of drastic increase, the conductivity once again levels off and is close to that of the filler material. This is at the percolation threshold where enough filler has been added so that it begins to form a continuous conductive network through the composite.

Many electrical conductivity models are proposed in the literature [21] based on various factors to predict the conductivity behavior of PNCs in order to achieve more efficient composite design that could result in desirable conductive PNCs. As these models based on theoretical and empirical equations are tuned to reproduce available experimental data they are applicable only near the critical transition point where the composite system moves from a perfect insulator to conductor, and when the matrix phase is a perfect insulator. Many researchers have studied simulation based approaches with electrical networks of fillers to predict the percolation and conductivity of composites with conductive fillers [22]. Though limited literature is available [23, 24] computational methods like finite element approach can predict electrical conductivity and percolation threshold of PNCs for various constituent morphology and properties. Monte Carlo methods are a broad class of computational algorithms that rely on repeated random sampling to obtain numerical solutions. Efficient percolation algorithms integrated with Monte Carlo methods are needed for developing RVE based design and analysis tools for electrical conductivity of nanocomposites.

Simulation results for electrical conductivity of Polyacrylonitrile (PAN) / CNT composite fibers spun using gel spinning [3] are developed in our research group [34] to demonstrate the design-analysis integrated models. Some of the electrical conductivity results are reviewed here. Both cylindrical and cubic RVE Models (Figure 22) are considered for analysis, maintaining desired volume fraction. RVE with a 3D network of CNTs within PAN fiber is modeled for a desired volume fraction with aspect ratio of 50-100 for CNTs. SEM image analysis and PDF are not used in the simulations for electrical and mechanical analysis of PNC fibers. In PNC fibers drawing induced exfoliation and orientation leads to the formation of a continuous conducting path within the polymer fiber [3]. A random orientation of CNT (± 20° along the drawing direction) is considered for generating a 3D network of CNT. The 3D network RVE models are exported to COMSOL^{TM} for quantifying the stress strain behavior and electrical conductivity of PNC using FEA.

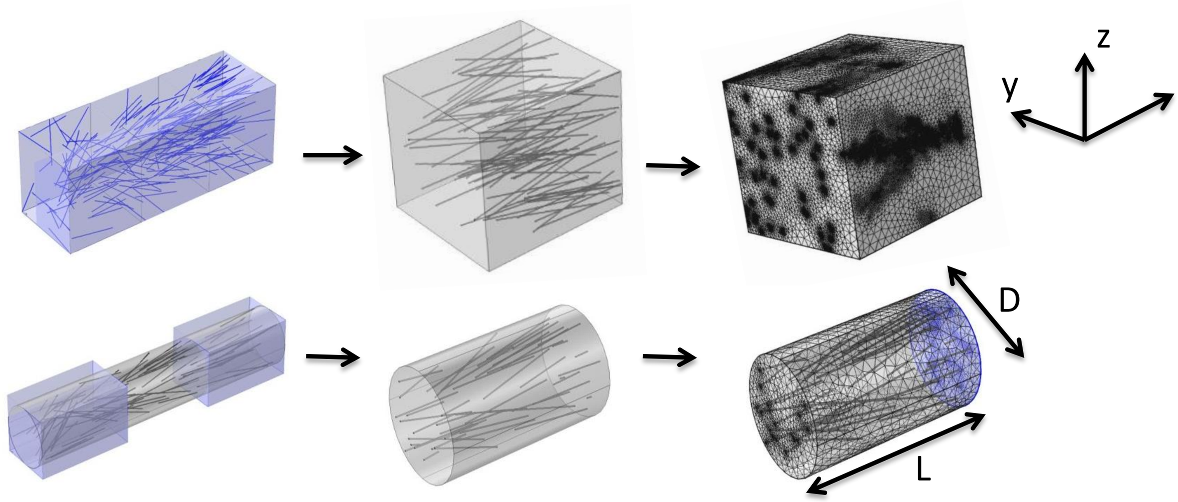
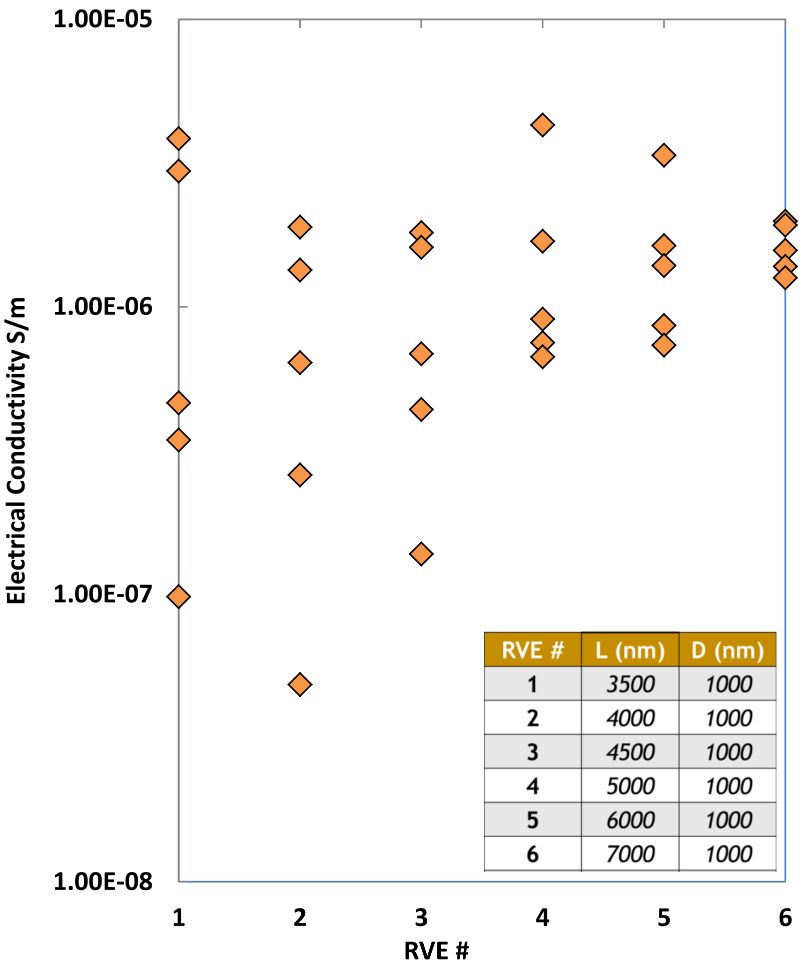


Figure 22. RVE Models for PAN/CNT Composite Fiber

RVE geometry is trimmed on both sides (X=0 and X=L), as shown in Figure 22, with a desired volume fraction for electrical conductivity analysis. This will allow CNT touching the surfaces of RVE, where applied *voltage* (at X=0) and *ground* (at X=L) boundary conditions are used. Tetrahedral mesh with CNT electrical conductivity of 10^6 S/m is used in the analysis. Figure 23 shows the variation of electrical conductivity of 0.57% volume fraction (1% weight fraction) CNT in composite fiber for various RVE sizes studied. As random variation of CNT within RVE is considered, the results from RVE models show variation in electrical conductivity values when the simulations were repeated five times, and the results are also sensitive to RVE size as shown in Figure 23. In these simulations the length of the RVE is selected based on the aspect ratio of the CNT considered, and the diameter is systematically changed to study the effect of RVE size on analysis results. As shown in Figure 23, RVE#6 showed less statistical variation in electrical conductivity results

Figure 23. Effect of RVE Size on Simulated Electrical Conductivity

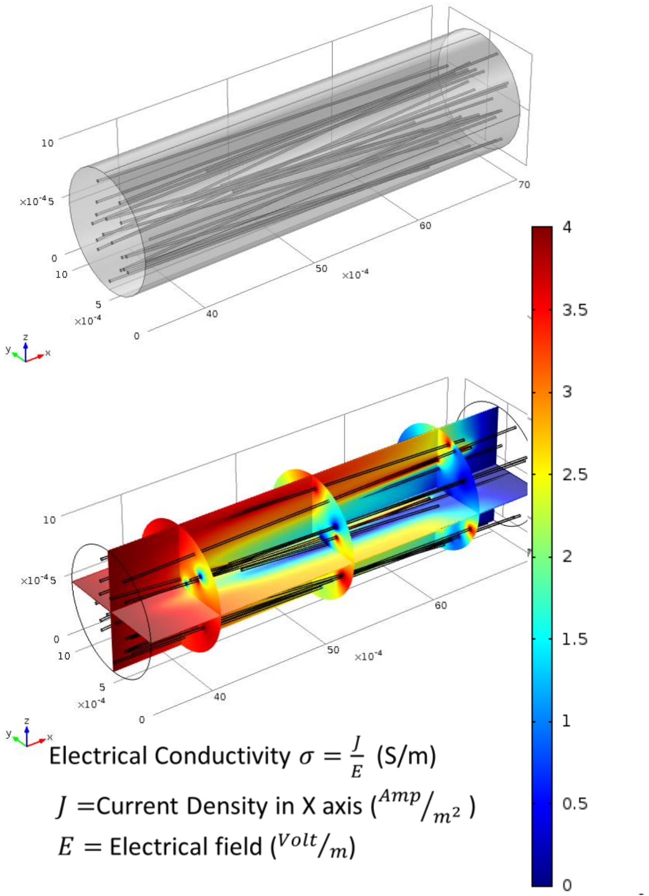


when simulations were repeated, indicating a more homogenized result.

The data points in Figure 23 represent electrical conductivity values obtained from five simulations for each RVE size to study the effect of RVE size on electrical conductivity. For a constant value of cylindrical RVE diameter D, the variation in electrical conductivity results reduced as RVE length L increased, and the variation in results is insignificant for RVE # 6 (L = 7000 nm) as shown in Figure 23. Figure 24 shows a contour plot of electrical potential (v) from which the electrical field (E) is determined. The electrical conductivity (σ) of PNC fiber is then determined from the current density (J) and electric field (E).

Experimental values for electrical conductivity of PAN/CNT fiber for various draw ratios ranges from $6.5x10^{-4} \pm 2.04x10^{-5}$ S/m [41]. Higher electrical conductivity in the experiments was attributed to the formation of more perfect conductive channels with increase in draw ratio [41].

Figure 24. Variation of Electrical (V) for an Applied Voltage at X=0 Plane



Electrical Conductivity Analysis using Resistor-Capacitor Approach

There are many different methods of electrically analyzing a CNT polymer nanocomposite. Among the various methods available in the literature, Resistor-Capacitor (RC) models [20] "replace" contacting CNTs with equivalent resistors and non-contacting CNTs with equivalent capacitors [42]. In this approach, an equivalent circuit is constructed by combining these equivalent resistors and capacitors in series and parallel based on how they relate to one another geometrically by contact within chains and the relationships between non-contacting chains of CNTs within the composite [42]. Furthermore, another factor that may affect the electrical conductivity is tunneling current present among CNTs that are very close, but not touching], and it may be useful to quantify these effects on the overall electrical conductivity within the equivalent circuit (see Figure 25). Once voltage is applied from one face of the composite within the model to another face, the current flowing through the composite can also be determined numerically and the electrical conductivity can be calculated [20].

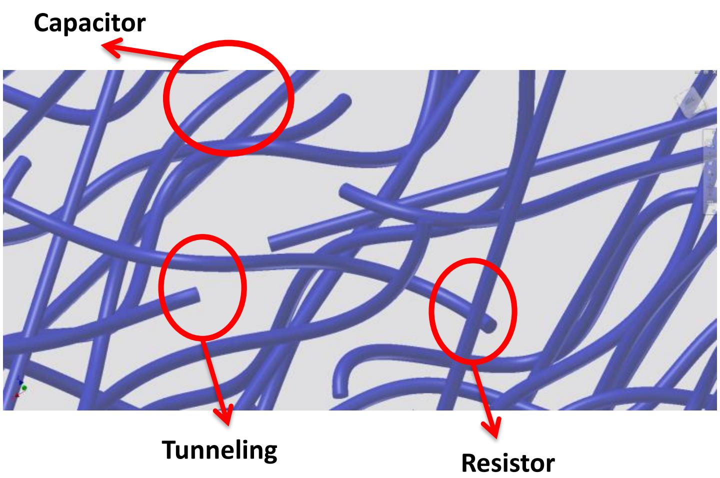


Figure 25: Equivalent circuit approach within RVE

The approach for this ongoing research include (i) Develop an algorithm to convert a 3D RVE with CNTs to an equivalent R-C network (ii) Develop the equivalent circuit procedure to work with both percolated and non-percolated RVEs. (iii) Solve for the composite electrical conductivity of the RVE using analytical approach (see Figure 26).

Role of Tunneling current in the overall electrical conductivity of Composite

When electrons hit a thin barrier, they behave like particles and bounces back. However, when large number of electrons hit the barrier, based on quantum mechanics, they behave like waves and some electrons penetrate the barrier, just like water penetrate through a dike. In analyzing the conductivity of a CNT-filled nanocomposite, because the penetrated electrons have motion, it contributes to the conductivity to the overall system. In a CNT-filled nanocomposite, each CNT fiber acts as the electron carriers throughout the entire system. When fibers make contact with one another, the electrons can transfer to the adjacent CNT fiber, but when fibers do not make contact, the space between the fibers becomes the barrier.

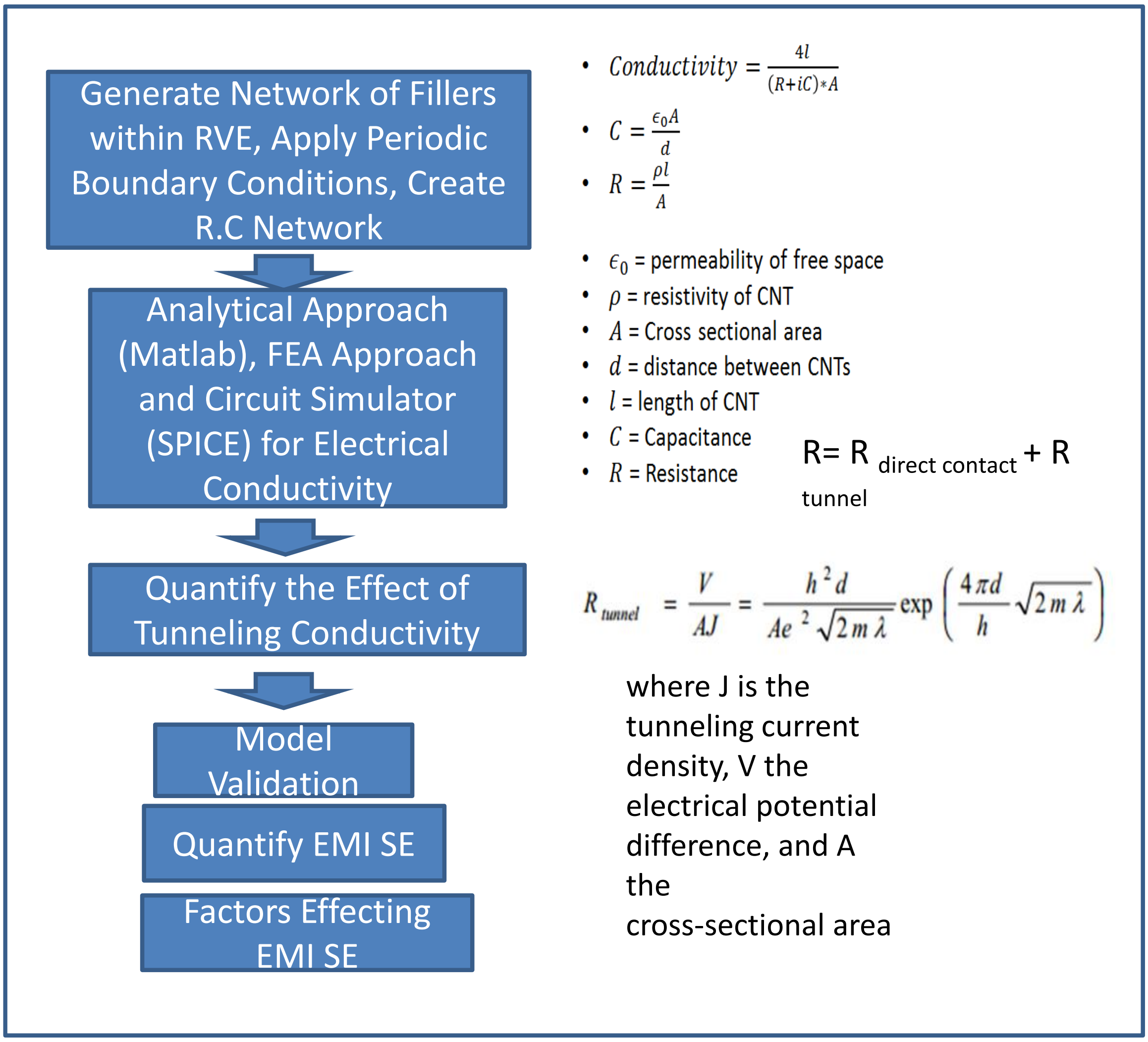


Figure 26: Approach to quantify EMI SE

When enough voltage is applied, ensuring enough electrons to pass through the RVE, tunneling current is generated. Factors that determine the tunneling conductivity can be known from analyzing the tunneling resistance, since tunneling conductivity is simply:

$$\boldsymbol{\sigma = \frac{1}{\rho}} \qquad\qquad \boldsymbol{\rho = R\frac{A}{\ell}}$$

Where $\boldsymbol{\sigma}$ is the conductivity, $\boldsymbol{\rho}$ the resistivity, R the resistance, A the cross sectional area, and $\boldsymbol{\ell}$ the length of CNT. Therefore, factors that influence the tunneling conductivity can be determined from tunneling resistance, which is expressed in:

$$\boldsymbol{R_{tunnel} = \frac{V}{AJ} = \frac{h^2 d}{Ae^2\sqrt{2m\lambda}}\exp\left(\frac{4\pi d}{h}\sqrt{2m\lambda}\right)}$$

Where J is the tunnel current density, V the electrical potential difference, e the quantum of electricity, m the mass of electron, h the Planck's constant, d the barrier width (distance between CNTs), λ the height of barrier(epoxy), and A the cross-sectional area of tunnel. Since e, m, and h are constants, factors that determine the tunneling resistance is: cross sectional area of CNTs and width and height of barrier of the epoxy. Since the cross sectional area for this research is considered constant throughout the CNT, effect of other two factors are considered.

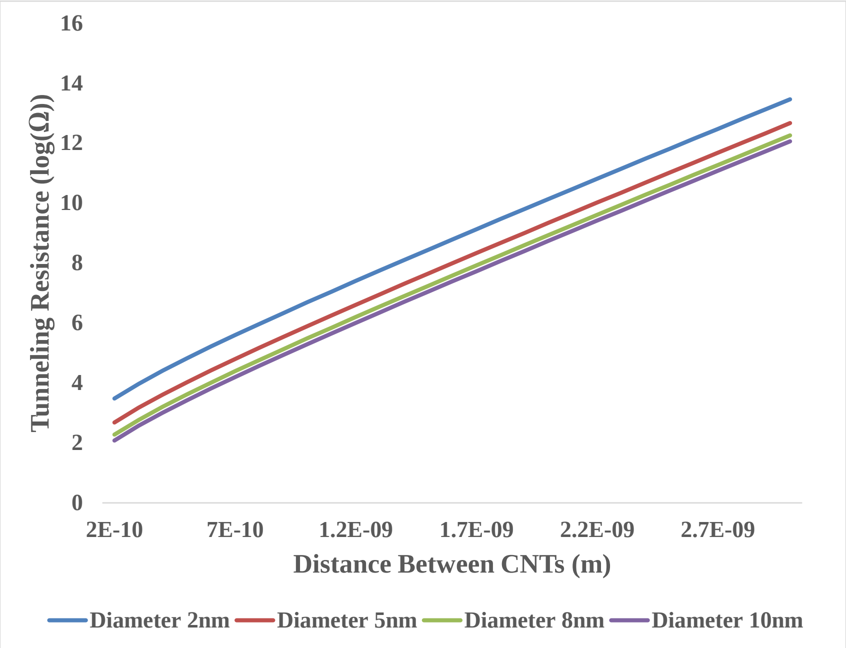


Figure 27: Effect of distance between CNTS on tunneling resistance

Quantifying the tunneling resistance for a given 3D network of fillers within RVE is currently in progress. Preliminary results indicate that tunneling conductivity decreases exponentially with respect to distance between the CNTs (barrier width) (see Figure 27) and decrease more exponentially in greater height of barrier (see Figure 28). The height of barrier is a constant that depends on the constituent materials within RVE. Also, tunneling resistance is greater in smaller diameter CNTs because greater diameter means bigger area of overlapping and thus easier tunneling effect.

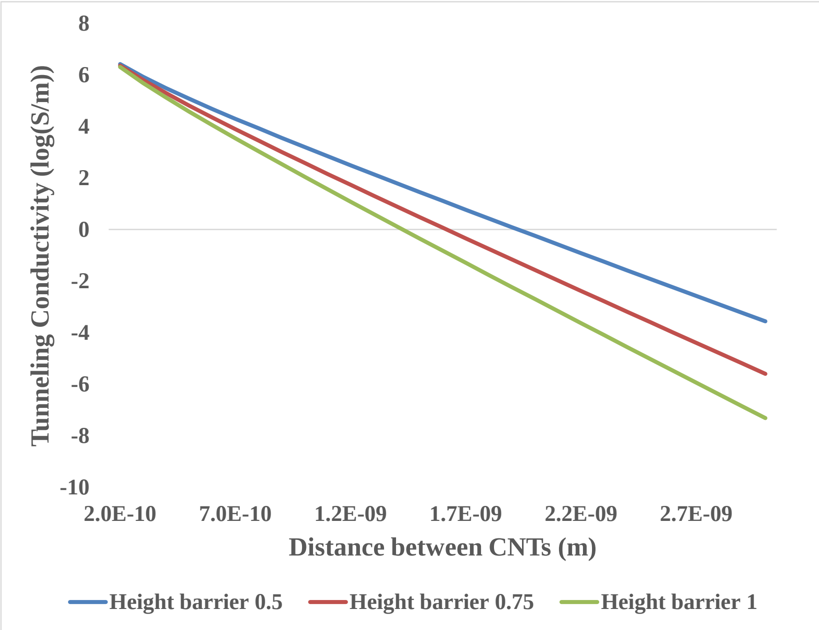


Figure 28: Effect of height of barrier on tunneling resistance

Conductivity and Electromagnetic Shield Effectiveness

Due to their light weight, versatility, low cost and processability, conductive polymer composites are attractive materials for use in enclosures for electronic and electrical devices to satisfy electromagnetic compatibility requirements. Electro Magnetic Interference (EMI) shielding is involved in many electronics applications. As electronics have increased in efficiency and decreased in size, components are more closely connected and the risk of interference has increased. A device is considered electromagnetically compatible with its surrounding if it does not interfere with other devices or itself, and it does not affected by emissions from other devices. Therefore, a good shielding material should prevent both incoming and outgoing electromagnetic interference (EMI).

Conventional conductive polymer composites made of stainless steel fibers, nickel coated carbon fibers are cost prohibitive for EMI applications because of the high concentration of filler required to achieve an adequate level of shielding. One tested method of improving shielding involves the use of CNT-polymer composites [43]. Various arrangements of these composites within a polymer can produce significant levels of shielding without compromising the conductivity of the composite system. Measuring conductivity through the use of nano composites can vary due to a variety of factors, such as agglomeration, single vs. multi-walled CNTs, arrangement and orientation, etc. At the same filler loading, polymer filled with nano-sized carbon filler has higher EMI Shielding Effectiveness (SE) [25] than polymer filled with micro-sized carbon filler. The EMI SE of a material is defined as the ratio of transmitted power to the incident power. The distance required by the power wave to be attenuated to 37% is defined as the skin depth. A good material for EMI shield should have high conductivity and high permeability along with a sufficient thickness to achieve the required number of skin depths.

The ongoing research in our group uses RVE models to quantify the electrical conductivity (σ) using 3D network based RVE models described in the previous sections. Based on the conductivity, the Electromagnetic Interference (EMI) Shielding Effectiveness (SE) can be calculated at different frequencies[44] as shown in Figure 29.

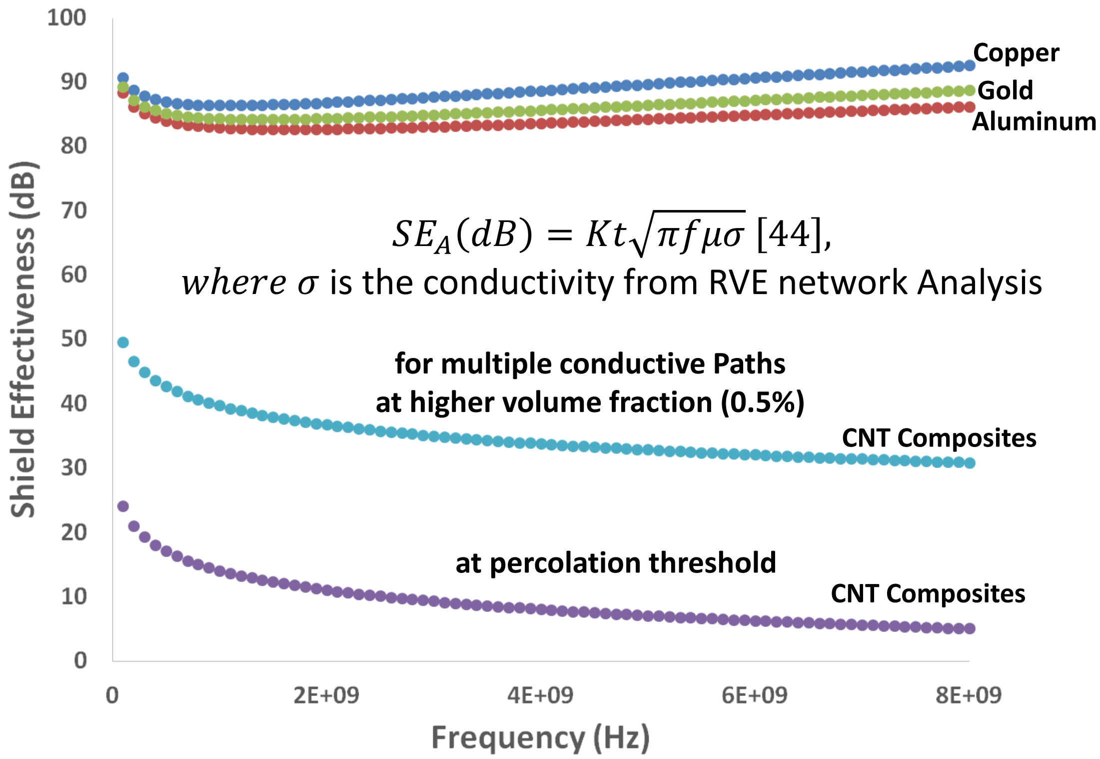


Figure 29: EMI SE of CNT Composites

As shown in Figure 29. Compared to metals, metal-filled composites, with a volume fraction as low as 0.5%, CNT composites can achieve EMI shield Effectiveness over 30 dB, which corresponds to 99.9 % attenuation of the EMI radiation.

CHAPTER 5

CONCLUSIONS

RVE models with material periodic conditions are developed in generating a 3D network of fillers within the RVE. Computational homogenization in 3D RVE models is achieved using two approaches. In the first approach, statistical analysis with number of realizations is performed with increasing RVE size of randomly generated CNT within polymer. In statistical analysis, the filler that exceeds the RVE are translated until they find new spatial location within RVE. Simulations with increasing RVE size are performed until the standard deviation of computed apparent property for each RVE size is minimum to predict the critical RVE size. In the second approach, RVE models with material periodic boundary conditions are developed, which involve placing fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE is part of a larger network of RVEs. Percolation threshold analysis of CNT filled polymer composites is presented using both computational homogenization approaches. It is demonstrated that computational homogenized models with material periodic conditions are independent of RVE size and provide homogenized results and are computationally efficient compared to statistical models.

Electro Magnetic Interference (EMI) shielding is involved in many electronics applications. An electronic device is considered electromagnetically compatible with its surrounding if it does not interfere with other devices or itself, and if it does not get affected by emissions from other devices. Computational tools are developed to quantify and optimize the EMI Shielding Effectiveness (SE) of carbon nanotube (CNT) composites. The approach involves developing 3D Representative Volume Element (RVE) models with CNTs within polymer block. The RVE models are converted in to an equivalent R-C network to determine the conductivity and further develop tools. To define the EMI SE is the main objective. The role of tunneling current in quantifying the electrical conductivity of composite is also considered. Preliminary results indicate that with a volume fraction as low as 0.5%, CNT composites can achieve EMI shield Effectiveness over 30 dB, which corresponds to 99.9 % attenuation of the EMI radiation.

Research Scope, Limitations and Future directions

Computational quantification of EMI Shielding Effectiveness can be calculated theoretically using conductivity of the material or computationally using computational models that allows analyzing the SE directly. However, the network-based CNT model has shown more challenges to quantify them in either way.

The conductivity using R-C network analysis can be done only in an ideal condition where all connections of fillers within an RVE is defined and characterized. However, the process of defining the percolation threshold or CNTs with multiple networks requires quantifying the conductivity as the filler is filled. Spanning from defining geometry, checking penetration with other existing fillers, and identifying contact networks, adding one filler for contact analysis is computationally expensive, and therefore an efficient algorithm to perform all of these tasks is essential. Instead of using a brute force method, implementing graph theory by classifying CNTs as points and contact points as dots and vertices was the most efficient algorithm that saved time by degree of hours. However, a more in-depth knowledge of graph theory needs to be understood and be implemented before performing analysis.

Due to the high aspect ratio, or ratio of length to diameter of the CNT, defining a universal mesh size is challenging and the presence of cusp formed between the filler and the boundary makes the mesh difficult to be defined in the finite element analysis. Additionally, the conductivity of composites cannot be defined accurately because the theoretical model assumes that CNTs within a certain distance are considered “touching”. When imported in computational program, the gap creates a resistance between CNTs and polymers, yielding a low composite conductivity. An alternative method needs to be implemented to the geometry such that all gaps are filled to make an actual connected network.

Publications

- W. Song, V. Krishnaswamy, & R.V. Pucha, "Computational Homogenization in RVE Models with Material Periodic Conditions for CNT Polymer Composites" *Composite Structures* vol. 137 (2016) p. 9-17
- W. Song, "EMI Shielding Effectiveness Analysis of CNT Composites" *The Tower*, Georgia Tech Undergrad Journal [Under Review]

Posters/Presentations

- R. Writhers, W. Song, "Stress Transfer in CNT Composites: Role of Interface and Interphase" Poster session presented at: *Undergraduate Research Opportunities Program Spring Symposium*, 2016 Apr. 19; Atlanta, GA
- M. Kurien, J. Seong, K. Lee, I. Kim, & W. Song, "Advanced Algorithms for Contact in RVE Models", Poster session presented at: *Undergraduate Research Opportunities Program Spring Symposium*, 2016 Apr. 19; Atlanta, GA
- W. Song, "Percolation, Electrical Conductivity and EMI Shield Analysis of CNT Composites" Poster session presented at: *Undergraduate Research Opportunities Program Spring Symposium*, 2015 Apr. 22; Atlanta, GA
- V. Krishnaswamy, W. Song, & I. Lakhia, "Seamlessly Integrated Design and Analysis tools for Nano-filler Composites" Oral Presentation at: *Undergraduate Research Opportunities Program Spring Symposium*, 2015 Apr. 22; Atlanta, GA
- P. Younes, & W. Song, "Role of boundary conditions in homogenized models for nanocomposites" Poster session presented at: *Undergraduate Research Opportunities Program Spring Symposium*, 2015 Apr. 22; Atlanta, GA
- W. Song, "Percolation, Electrical Conductivity, and EMI Shield Analysis of CNT Composites" Poster session presented at: *Air Products Symposium*, 2015 Apr. 3; Atlanta, GA
- H. Littmann, K. Hansen, P. Younes, & W. Song, "Developing an Efficient Algorithm to Calculate Percolation Threshold" Poster session presented at: *Undergraduate Research Opportunities Program Spring Symposium*, 2014 Apr. 22; Atlanta, GA
- K. Hansen , H. Littmann, P. Younes, & W. Song, "Electrical Conductivity Analysis of CNT Composites" Poster session presented at: *Air Products Symposium*, 2014 Apr. 22; Atlanta, GA

Awards and Recognition

- UROP Outstanding Undergraduate Researcher 2016 (School of Mechanical Engineering)
- 2nd place oral presentation award in among all engineering departments in annual Undergraduate Research Opportunities Symposium, Spring 2015
- Air Products Undergraduate Research Award Recipient, Spring 2015
- *President's Undergraduate Research Award* , Summer 2015
- *President's Undergraduate Research Award* , Spring 2016

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