TRANSPORT PROPERTIES OF NANOCOMPOSITES

A Thesis

by

VINAY NARAYANUNNI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2010

Major Subject: Mechanical Engineering

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Approved by:

Chair of Committee,	Choongho Yu
Committee Members,	Dong Hee Son
	N K Anand
Head of Department,	Dennis O' Neal

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ABSTRACT

Transport Properties of Nanocomposites. (May 2010)

Vinay Narayanunni, B.Tech., National Institute of Technology

Chair of Advisory Committee: Dr. Choongho Yu

Transport Properties of Nanocomposites were studied in this work. A Monte Carlo technique was used to model the percolation behavior of fibers in a nanocomposite. Once the percolation threshold was found, the effect of fiber dimensions on the percolation threshold in the presence and absence of polymer particles was found. The number of fibers at the percolation threshold in the presence of identically shaped polymer particles was found to be considerably lower than the case without particles. Next, the polymer particles were made to be of different shapes. The shapes and sizes of the fibers, as well as the polymers, were made the same as those used to obtain experimental data in literature. The simulation results were compared to experimental results, and vital information regarding the electrical properties of the fibers and fiber-fiber junctions was obtained for the case of two stabilizers used during composite preparation – Gum Arabic (GA) and Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). In particular, the fiber-fiber connection resistances, in the case of these 2 stabilizers, were obtained. A ratio between the fiber path resistance and the total connection resistance, giving the relative magnitude of these resistances in a composite, was defined. This ratio was found through simulations for

different fiber dimensions, fiber types and stabilizers. Trends of the ratio with respect to composite parameters were observed and analyzed, and parameters to be varied to get desired composite properties were discussed. This study can serve as a useful guide to choose design parameters for composite preparation in the future. It can also be used to predict the properties of composites having known fiber dimensions, fiber quality and stabilizing agents.

DEDICATION

I would like to dedicate this work to myself.

ACKNOWLEDGEMENTS

I would like to sincerely thank my parents, for their unconditional support and encouragement throughout my master's degree. I would like to thank my advisor, Dr. Choongho Yu for imparting his academic and non-academic wisdom; and for numerous intellectually stimulating discussions. I take this opportunity to thank my thesis committee members, Dr. N K Anand and Dr. Dong Hee Son for their valuable time and help with the thesis.

I would also like to thank my friends and family members who supported me in times of need.

NOMENCLATURE

Variables

f_c	Critical volume fraction
f	Volume fraction of the conductive phase
ct	Conductive exponent
$2L$	Normalized fiber length
D	Normalized fiber diameter
x	Cartesian co-ordinate along x direction
y	Cartesian co-ordinate along y direction
z	Cartesian co-ordinate along z direction
t	Scalar parameter less than or equal to L
s	Scalar parameter less than or equal to L
u	Distance vector between two fibers
F	Square of the distance between the fibers
d	Distance between two fibers
N	Total number of fibers
n	Number of connections
R	Resistance
l	Length of percolation path
A	Fiber area

Length	Length of the composite
Area	Area of the composite face

Greek symbols

σ	Electrical conductivity
α	Zenith angle of fiber
θ	Azimuth angle of the fiber
π	Pi

Subscripts

1	Corresponding to fiber arm 1
2	Corresponding to fiber arm 2
m	Variable taking values 1 or 2
n	Variable taking value 1 or 2
i	Corresponding to fiber i
j	Corresponding to fiber j
0	Corresponding to initial or minimum value
min	Minimum
c	Connection
f	Fiber
fp	Fiber path
Total	Total
Composite	Composite

Ratio	Ratio

Superscripts

i	Corresponding to fiber i
j	Corresponding to fiber j

Acronyms

GA	Gum Arabic
PEDOT: PSS	Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
CNT	Carbon nanotube
TIM	Thermal interface material
UPR	Unsaturated polyester resin
SEM	Scanning electron microscopy
MC	Multiplicative congruential
CVF	Critical volume fraction

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1. INTRODUCTION

1.1 Carbon nanotube (CNT) network polymer composites

At present, the efficiencies of thermoelectric devices are not competent enough to completely replace conventional power generation and refrigeration systems. In spite of this, thermoelectric devices are popular due to their simple structure, lack of moving parts, noiseless operation and higher power densities (power per unit weight or volume) than conventional power sources. The inability to increase thermoelectric efficiencies over the past years, have led researches to search for new materials and devices that have better power densities. For instance, if conventional thermoelectric materials were to be replaced by polymers, there is potential for the power density to be increased by approximately six or seven times due to the low density of polymers($\approx 1.2 g/cm^3$).[1] Polymers are cheap and easy to manufacture. Polymers also have low thermal conductivities. This is a very desirable property to increase the thermoelectric figure of merit. On the down side, polymers have extremely low electrical conductivities which can drastically decrease the thermoelectric efficiency. Due to the high power densities, it may still be profitable to use polymers, and, the use of polymer composites may be the solution to the problem of low efficiency.

Composites are structures made of materials which maintain their identities even after the component is formed fully. The properties of the composites will be a

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This thesis follows the style of *International Journal of Heat and Mass Transfer*.

combination of the properties of its individual constituents. The constituent materials can be of two types. The ‘matrix’ and the ‘reinforcement’. The matrix material surrounds and supports the reinforcement materials. The reinforcement materials have physical properties which make up for the inferior properties of the matrix and enhance the properties of the composite.

The matrix in the polymer composite is the polymer. Different kinds of reinforcements can be used along with the polymer. There are a variety of materials which can serve as reinforcements. High electrical conductivity is a mandatory requirement of the reinforcement material in order to counter the low electrical conductivity of polymers, consequently increasing the figure of merit. Metals, Carbon nanotubes etc. are possible candidates. Metals have high density, and hence tend to increase the weight of the composites. The inclusion of metals also makes the composites less flexible. Carbon nanotubes on the other hand, are light weight and this helps to maintain the high power density. Carbon nanotubes also have high strength and flexibility.

Carbon nanotubes were discovered by Iijima in 1991.[2]Carbon nanotubes posses many desirable properties. They have extremely high tensile strength and Young’s modulus. They have high electrical and thermal conductivities and good optical properties. Carbon nanotubes are generally classified into single walled and multiwalled nanotubes. Single walled nanotubes consist of a single graphite sheet seamlessly wrapped into a cylindrical tube. Multiwalled nanotubes comprise an array of such

nanotubes that are concentrically nested. CNTs have many applications. They are being used in electrochemical devices, for hydrogen storage, field emission devices, nanometer-sized electronic devices, sensors and probes.[3]

The reinforcements can be in the form of particles, whiskers (very fine single crystals), short fibers, long fibers etc. Long fibers make it difficult to produce complex shapes of composites containing them. If the reinforcements are particles, there is lack of connection between them which diminishes the electrical conductivity. Short fibers are ideal for establishing good connection between the fibers without compromising on the weight, flexibility and the ability to be made into different shapes.

Polymer matrix composites embedded with conducting fibers are known to exhibit an insulator to conductor transition at a certain volume fraction of fibers ((volume of fibers)/ (Total composite volume)) called the critical volume fraction f_c. This is also known as the percolation threshold and is understood by the percolation theory.[4] Figure 1 gives a representation of this effect.

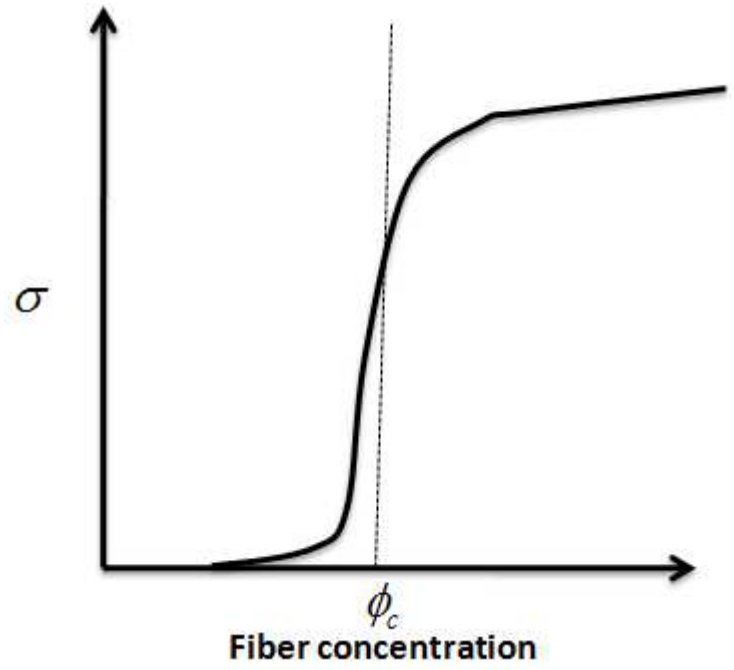

Figure 1 Change in electrical conductivity with fiber volume fraction

Materials having high electrical conductivities usually have high thermal conductivities. The same is true in the case of carbon nanotubes. High thermal conductivity leads to a low thermoelectric figure of merit. Experimental studies have shown that the thermal conductivity does not increase as steeply as the electrical conductivity at the percolation threshold. Carbon nanotubes in the form of short fibers embedded in the polymer are one dimensional nanomaterials. Since the dimensions are of the order of nanometers, the contact area between the connected fibers is very low. The low contact area is detrimental to effective heat transfer, but the electrons travel from one fiber to another leading to effective electrical transport. So, the high value of

electrical conductivity and relatively low value of thermal conductivity tends to increase the thermoelectric figure of merit.

1.1.1 Applications and prospects

Polymer matrix composites are popular in the aerospace industry due to their stiffness lightness and heat resistance. They are also being used as Thermal Interface Materials (TIMs) which connect semiconductor chips and electronic components to a heat sink. Gel type polymer TIM systems embedded with carbon fibers are popular as they conform well to the surface irregularities of the chip and the heat sink, resulting in uniform heat transfer and very low thermal resistance. Since these TIMs are polymers, they also help to protect the chips from mechanical stresses, by acting as a shock absorber. As mentioned before, CNT network polymer composites can serve as light weight, thermoelectric materials.

1.1.2 Objectives

Create a computational model which initially creates a virtual volume representing the volume of the CNT network polymer composites; embeds the virtual volume with CNT fibers using the Monte-Carlo technique and then develops connection criteria between the fibers to ensure the presence of a CNT fiber network inside the polymer capable of transporting electricity and heat across the composite. Find the volume fraction of fibers in the composite needed to reach percolation threshold (Critical Volume Fraction) for different fiber lengths, fiber diameters and fiber aspect ratios. Find

the number of fiber connections in each case and use established equations to find electrical conductivity of the composites.

2. LITERATURE REVIEW

Experimental studies on electrical conductivity of conducting fiber in polymer composites suggest that the electrical conductivity follows power law dependence with respect to fiber concentration.[1, 5-11] Percolation theory has been successful in explaining this phenomenon. The basic concept of percolation theory lies in the determination of how a given set of sites (nano fibers in this case) is interconnected by means of a bonding criterion.[12] The network of interconnected sites is termed as a cluster. If the cluster connects the ends of the composite, then it is termed as a percolation cluster and it forms a pathway for electrical conduction. The minimum concentration of fibers needed to form this kind of pathway is called the percolation threshold or the critical volume fraction. The electrical conductivity of the fiber network composite after the percolation threshold is given by[4, 13]

$$\sigma_c = \sigma_o (f - f_c)^{ct} \tag{1}$$

Here σ_c is the total conductivity of the polymer composite. σ_o is the pre-exponential constant, which normally is equal to the conductivity of the conductive phase (nano fiber in this case). f is the volume fraction of the conductive phase and f_c is the critical volume fraction of the conductive phase. ct is the conductive exponent. The goal of this work is to develop a computational model to explain percolation and electrical conductivity in CNT network polymer composites.

The Monte Carlo technique[14, 15] is a popular technique used to solve percolation problems and is used in this work. The technique relies on the use of random

numbers which makes it an effective tool to simulate the random arrangement of fibers in the polymer. Once the random fibers are created, a connection criterion between them is defined. All the connected fibers are checked to see if they form a percolation cluster which enables energy transport.

The groundwork for solving percolation problems using the Monte Carlo technique was laid in 1974 by Pike and Seager.[12] They did a 2 D study and the fibers were modeled as sticks of zero width and a fixed length. A constant number of sticks were embedded in the volume representing the composite and the length of the stick was varied to find the minimum length leading to percolation. The number of bonds per site; that is, the number of connections per stick was also found out. Balberg et al. in 1983 developed a model based on the work of Pike and Seager.[16] They made the 2D system isotropic by randomly orienting the sticks and also made the length of the sticks unequal. The cluster resistance was also obtained as a function of stick length. Du et al. in 2005 did a 2D Monte Carlo study of CNT composite percolation conductivity using a zero width stick system.[9] They found that the electrical conductivity follows a power law not only with concentration, but also the alignment angle of the sticks. Natsuki et al. in 2005 assigned a finite width to the sticks and performed a 2 D study using Monte Carlo technique to find the percolation behavior in fiber reinforced composites.[17] Critical volume fraction was reported as a function of fiber aspect ratio and orientation angle of the fiber. Wu et al. in 2006 did a 2 D Monte Carlo study similar to Natsuki's work and obtained the solution of percolation problem on oriented short-fiber composites which was used to explain experimental electrical conductivity data of CNT/Unsaturated

polyester resin (UPR) nanocomposites.[7] The critical volume fraction as a function of aspect ratio and the electrical conductivity as a function of volume fraction of the fibers are reported. The possibility of electrical conduction through the fibers by electron hopping and electron tunneling is also discussed.

3 D studies are expected to give a much more realistic picture when comparing with experimental data. Sur et al. in 1976 did Monte Carlo studies of percolation phenomena for a simple cubic lattice, applicable mainly to disordered binary alloys.[18] The earliest 3 D Monte Carlo study applicable to fiber composites was done by Balberg et al. in 1984.[19] The effects of aspect ratio of the sticks and macroscopic anisotropy on the percolation threshold were reported. Taya et al. in 1987 did a 3 D percolation study to predict the in-plane electrical conductivity of misoriented short fiber composites. The sticks were considered to be capped cylinders. Percolation threshold as a function of aspect ratio and electrical conductivity as a function of volume fraction for different aspect ratios were reported. Lee and Kim in 1995 did a study on the percolation behavior and electrical conductivity in unidirectional composites made of short conductive fibers in insulating matrix by Monte Carlo simulation as a function of aspect ratio, volume fraction and angle. The lengths of the fibers were kept fixed in one case and normally distributed in another case. It was found that the percolation threshold is independent of the fiber length distribution. Ounaies et al. in 2003 did a 3 D percolation study considering the fibers as cylinders to explain the electrical properties of single wall carbon nanotube reinforced polyimide composites.[8] Foygel et al. in 2005 did a 3 D Monte Carlo percolation study of carbon nanotube composites and suspensions by

considering the fibers as randomly oriented sticks.[20] The critical volume fraction as a function of length of fiber, diameter of fiber and aspect ratio of fiber were reported. The electrical conductivity as a function of the fiber volume fraction was also reported.

The works mentioned above modeled the fibers as straight sticks. This is rarely the case in reality as seen in the SEM images.[1, 6, 7] The CNTs are flexible and they remain twisted curled, entangled and compressed in the composites. Yi et al. in 2004 developed a 3 D Monte Carlo model which took into consideration the effect of fiber waviness on the percolation threshold.[21] It was found that the percolation threshold increased with the curl ratio of the fiber. A general methodology for characterizing non-straight finite width fibers including kinked or curly fibers was developed. Three different fiber shapes; sinusoidal, triangular and rectangular were studied and it was found that the percolation threshold does not vary much between these fiber shapes if their curl ratio remained the same. Although this model is more effective in modeling nanofibers than the stick model, it is mathematically complex. Dalmas et al. in 2006 did a 3 D numerical simulation using finite element method to find electrical conductivity in entangled fibrous networks in order to be compared with experimental electrical conductivity data of multi wall nanotube polymer nanocomposites.[6] A study on the effect of aspect ratio and critical volume fraction for straight and tortuous fibers was done. Although this is a more accurate representation of the real scenario and a better model than the straight stick system, the size in width of the fibers was ignored.

The fiber models of Yi et al. and Dalmas et al. may be difficult to execute when the polymer particles in the composite has also to be taken care of during the simulation. Gao and Ma in 2008 developed a 3 D Monte Carlo model which took into account both the fiber thickness and fiber flexibility. Although this model is simple and simulates the real scenario efficiently, the effect of polymer particles in the composite was not considered.[22]

There has not been much work done to simulate the properties of fiber polymer composites which take into account the effect of polymer particles. In this work, the presence of polymer particles in the composites is considered and Gao's model is adopted to explain the properties of CNT network polymer composites.

3. METHODOLOGY

The modeling of the percolation phenomena in CNT network polymer composites involves two steps. In the first step, the CNT fibers are modeled and randomly placed in a non-dimensional cube of unit length. This random placement represents the actual arrangement of fibers in the composite. The second step involves developing a connection criterion between the fibers. This connection criterion allows the determination of fiber networks and ultimately in the detection of percolation clusters in the composite.

The CNT fiber is modeled as shown in Figure 2[22]. The fiber has two segments of length L and diameter D. The two segments or the arms of the fiber can pivot about the connection point at the centre.

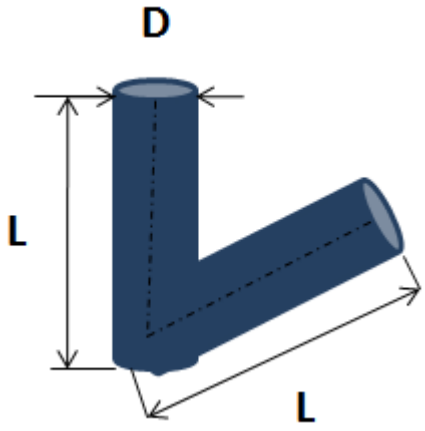

Figure 2 CNT represented as an arm shaped fiber

The position, shape and orientation of the fibers are defined by means of a global and local coordinate system as shown in Figure 3.[22]

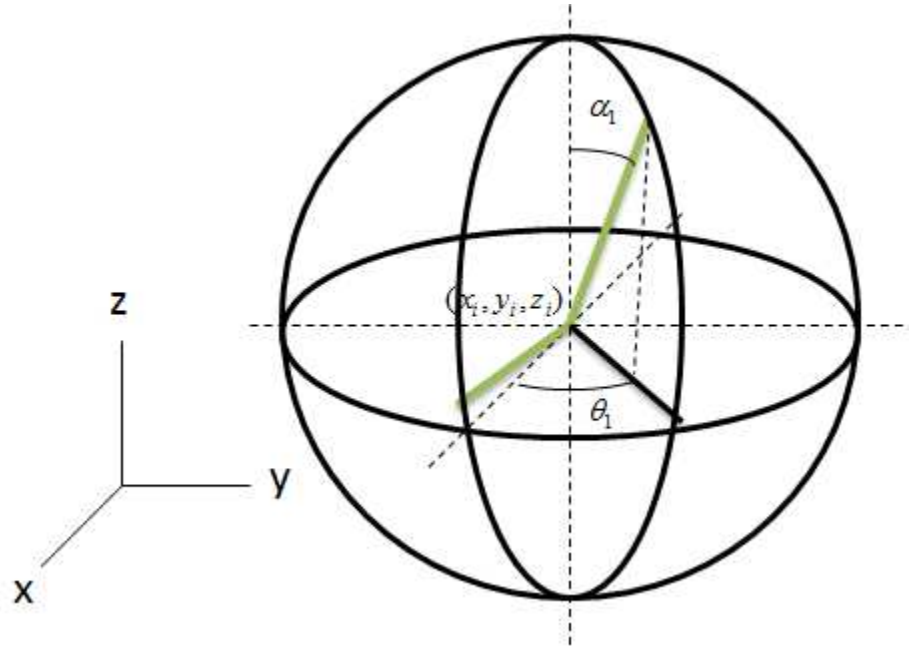

Figure 3 Fiber parameters defined by a global and a local coordinate system

The center or the vertex of the *i*th fiber (x_i, y_i, z_i) is defined with respect to the global Cartesian coordinate system. A local spherical coordinate system is attached to the fiber with the center of the coordinate system coinciding with the center of the fiber. The zenith angles α_1^i and α_2^i define the position of arms 1 and 2 respectively in the vertical

plane. The azimuth angles θ_1^i and θ_2^i define the horizontal position of arms 1 and 2 respectively. Any point (x, y, z) on arm 1 is given by

$$\begin{Bmatrix} x \\ y \\ z \end{Bmatrix} = \begin{Bmatrix} x_i \\ y_i \\ z_i \end{Bmatrix} + t \begin{Bmatrix} \cos\theta_1^i \sin\alpha_1^i \\ \sin\theta_1^i \sin\alpha_1^i \\ \cos\alpha_1^i \end{Bmatrix} \tag{2}$$

Similarly, any point (x, y, z) on arm 2 is given by

$$\begin{Bmatrix} x \\ y \\ z \end{Bmatrix} = \begin{Bmatrix} x_i \\ y_i \\ z_i \end{Bmatrix} + t \begin{Bmatrix} \cos\theta_2^i \sin\alpha_2^i \\ \sin\theta_2^i \sin\alpha_2^i \\ \cos\alpha_2^i \end{Bmatrix} \tag{3}$$

t is a scalar parameter, which less than or equal to half the fiber length. The length of the representative volume element (RVE), that is, the average size of the CNT polymer composite is used as the normalizing parameter. So, the volume representing the composite becomes a cube of unit length. The fibers are randomly distributed in this unit cube as shown in Figure 4.[22] Here, $x_i \in [0,1]$, $y_i \in [0,1]$, $z_i \in [0,1]$, $t \in [0, L]$, $\alpha_1^i \in [0, \pi]$, $\theta_1^i \in [0, 2\pi]$, $\alpha_2^i \in [0, \pi]$ and $\theta_2^i \in [0, 2\pi]$. x_i, y_i, z_i, α_1^i, α_2^i and θ_1^i are generated randomly. If θ_1^i is less than or equal to π, then, θ_2^i is given by $\theta_1^i + \pi$. If θ_1^i is greater than π, then θ_2^i is given by $\theta_1^i - \pi$. The diameter D and the length L are user defined. Thus the fiber is defined by six random numbers. In order to generate random numbers, a multiplicative congruential (MC) random number generator is adopted.

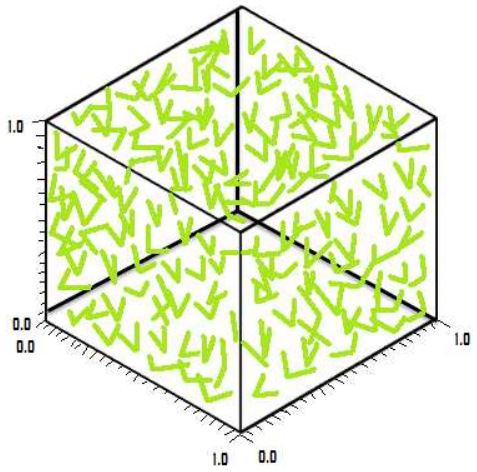

Figure 4 Fibers distributed randomly in a unit cube

In addition to the six random numbers which define the parameters of the fiber, the fiber is also assigned a fiber number and a cluster number. The fiber number is assigned to identify the fiber and the cluster number is meant to mark the percolation cluster or network to which the fiber belongs.

Percolation pathways are formed when fibers intersect with each other and from a network connecting the ends of the composite. Generally, three kinds of connections are possible between fibers as shown in Figure 5. These are body to body, end to end, and end to body.

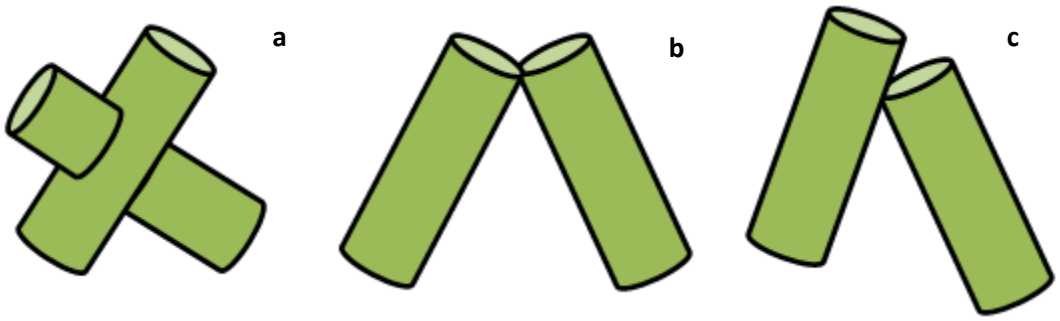

Figure 5 Different types of connections between fibers

It has been shown that the fraction of end to end, and end to body connections as compared to the total number of connections is very less. Moreover, these two types of connections take more time to model than the body to body connections.[22] In this work only the body to body connections are taken into consideration while modeling the percolation phenomena.

Consider the connection between two fibers say the 'ith fiber' and the 'jth fiber'. Let the 'jth fiber' be represented by equation (4)

$$\begin{Bmatrix} x \\ y \\ z \end{Bmatrix} = \begin{Bmatrix} x_j \\ y_j \\ z_j \end{Bmatrix} + s \begin{Bmatrix} \cos\theta_n^j \sin\alpha_n^j \\ \sin\theta_n^j \sin\alpha_n^j \\ \cos\alpha_n^j \end{Bmatrix} \tag{4}$$

Here $s \in [0, L]$. Figure 6 represents fiber i and fiber j and the distance between them at random points t and s on fiber i and fiber j respectively.

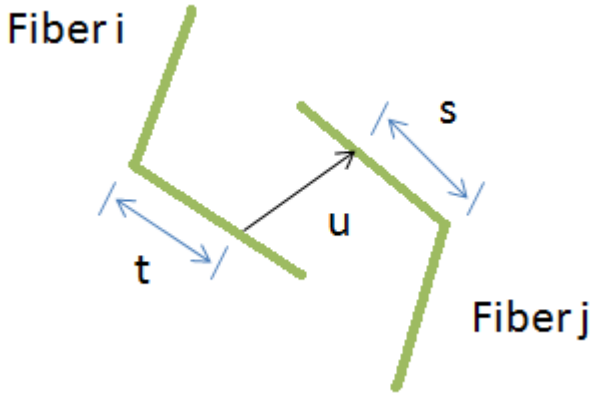

Figure 6 Distance between the ith and the jth fibers

The square of the distance between a point on the ith fiber and a point on the jth fiber is obtained from equations (2), (3) and (4) given by

$$F = u \cdot u \tag{5}$$

Here u is given by

$$\begin{aligned} u = {} & (x_i - x_j + t\cos\theta_m^i \sin\alpha_m^i - s\cos\theta_n^j \sin\alpha_n^j)e_1 \\ & +(y_i - y_j + t\sin\theta_m^i \sin\alpha_m^i - s\sin\theta_n^j \sin\alpha_n^j)e_2 \\ & +(z_i - z_j + t\cos\alpha_m^i - s\cos\alpha_n^j)e_3 \end{aligned} \tag{6}$$

Here $m = 1, 2$ and $n = 1, 2$. From equation (5) and equation (6), we obtain

$$F = t^2 + C_1 t + C_2 ts + s^2 + C_3 S + C_4 \tag{7}$$

$$\begin{aligned}
C_1 &= 2\Delta x \cos\theta_m^i \sin\alpha_m^i + 2\Delta y \sin\theta_m^i \sin\alpha_m^i + 2\Delta z \cos\alpha_m^i \\
C_2 &= -2[\sin\alpha_m^i \sin\alpha_n^j \cos(\theta_m^i - \theta_n^j) + \cos\alpha_m^i \cos\alpha_n^j] \\
C_3 &= -2\Delta x \cos\theta_n^j \sin\alpha_n^j - 2\Delta y \sin\theta_n^j \sin\alpha_n^j - 2\Delta z \cos\alpha_n^j \\
C_4 &= (\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2 \\
\Delta x &= x_i - x_j, \Delta y = y_i - y_j, \Delta z = z_i - z_j
\end{aligned} \tag{8}$$

F is the square of the distance between the fibers. F is a function of the variables t and s. We are interested in the points on the two fibers, that is the values of t and s which give the minimum value of F. For this we differentiate F each with t and s set the resultants equal to zero.

$$\frac{\partial F}{\partial t} = 2t + C_1 + C_2 s = 0 \tag{9}$$

$$\frac{\partial F}{\partial s} = 2s + C_3 + C_2 t = 0 \tag{10}$$

Simultaneous solution of equations (9) and (10) gives

$$t_0 = \frac{2C_1 - C_2 C_3}{C_2^2 - 4} \tag{11}$$

$$s_0 = \frac{2C_3 - C_1 C_2}{C_2^2 - 4} \tag{12}$$

For t_0 and s_0 to represent the points on the fibers representing the minimum distance between them, it is necessary that the conditions given in equation (13) are also satisfied.

$$\frac{\partial^2 F}{\partial t^2} > 0, (\frac{\partial^2 F}{\partial t^2})(\frac{\partial^2 F}{\partial s^2}) - (\frac{\partial^2 F}{\partial t \partial s})^2 > 0. \quad (13)$$

From equation (7) , it is clear that

$$\frac{\partial^2 F}{\partial^2 t} = 2 > 0 \quad (14)$$

and

$$(\frac{\partial^2 F}{\partial t^2})(\frac{\partial^2 F}{\partial s^2}) - (\frac{\partial^2 F}{\partial t \partial s})^2 = 4 - C_2^2 > 0 \quad (15)$$

Equation (14) and equation (15) hold as long as the fibers are not parallel to each other, that is as long as $\alpha_m^i \neq \alpha_n^i ; \theta_m^i \neq \theta_n^j$. So in the case of non parallel fibers, F has a minimum value for values of t_0 and s_0 given in equations (11) and (12) respectively.

In this work, the random number generator produces numbers with a large number of decimal places. So, the chances of having considerable number of parallel fibers during the simulation are very less. Using the values of t_0 and s_0, the minimum distance, $d_{\min}$ for non parallel fibers is calculated as

$$d_{\min} = (\frac{C_2^2 C_4 + C_1^2 + C_3^2 - C_1 C_2 C_3 - 4C_4}{C_2^2 - 4})^{1/2} \quad (16)$$

If the minimum distance is less than or equal to the diameter of a fiber, then the fibers are assumed to be connected. To be more precise, the ith and the jth fiber are said to be connected, when $d_{\min} \leq D$ along with the conditions, $0 \leq t_0 \leq L$ and $0 \leq s_0 \leq L$.

3.1 Implementation of the code

A Fortran 90 code is executed with the system supported by the supercomputing facility at the Texas A and M University. The simulation is done within a space enclosed by a unit cube as mentioned before. The random numbers generate the fiber parameters and the fibers are distributed in the cubic space. Fiber numbers from 1 to N are assigned to the fibers, where N is the total number of fibers. In the beginning, the cluster number of each fiber is set to be equal to the fiber number of that fiber. As the next step, two arrays are defined. One of them stores the fiber numbers at the top boundary of the composite and the other stores the fiber numbers at the bottom boundary of the composite. Next, the connectivity between the fibers is checked in a systematic manner. The first fiber is taken and it is checked for connectivity with the second fiber. If they are connected, then, the cluster number of the second fiber is set as the cluster number of the first fiber. Irrespective of whether the first and the second fiber are connected, the first fiber is next checked for connectivity with the third fiber and so on till the Nth fiber. This process is done for all the N fibers. In general, the fiber I is checked with fiber i+1 for connectivity and if they are connected, then both the fibers are assigned the lower cluster number among the two. So in a connected network or a percolation pathway, all the fibers in the cluster will have the same cluster number. Percolation or the formation of a pathway connecting the top and bottom of the composite is detected by checking if the cluster number of any of the fibers at the top of the composite and any of the fibers at the bottom of the composite are same. The Critical Volume Fraction (CVF) is the

fraction of total fiber volume to the total composite volume at the instance of the first percolation.

4. RESULTS AND DISCUSSION

In all the simulations, the representative volume element (RVE) is taken to be of size 20 μm . L is the normalized half fiber length normalized with the size of the RVE. D is the normalized diameter normalized with respect to the size of the RVE. So, the volume fraction of the fibers is given as $2NL\pi D^2 / 4$. The critical volume fraction (CVF) is obtained when N is the number of fibers at the percolation threshold. The CVF depends on the fiber dimensions and the number of fibers.

4.1 Effect of fiber length

The length of the fiber plays an important role in determining the CVF. Figure 7 shows the variation of the critical volume fraction with respect to the lengths at fixed diameter of the fiber. The lengths of the fibers considered in this case are 4 μm , 5 μm , 6 μm , 7 μm and 8 μm which yield L values of .1, .125, .15, .175 and .2 respectively. The diameters considered are 100nm, 250nm and 400nm which yield D values of .005, .0125 and .02 respectively. Results are taken for 10 runs of the program for each of these fiber dimensional parameters. Average values obtained from these 10 repetitions.

It is seen from Figure 7 that the critical volume fraction decreases with increasing fiber length for a given diameter. This trend is consistent with previous works, for instance with Foygel's work.[20] This trend also seems logical because, with

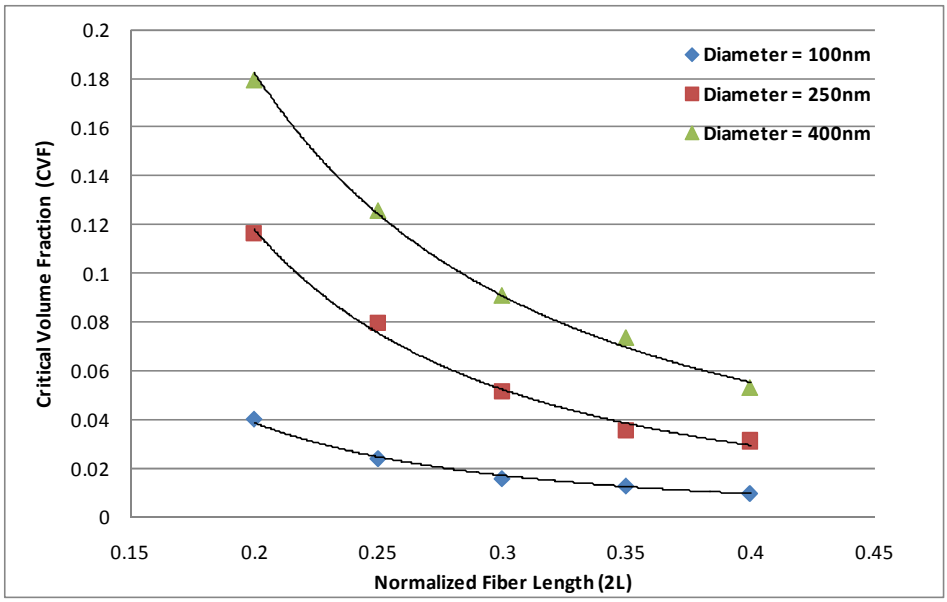

Figure 7 Critical volume fraction versus normalized fiber lengths for different fiber diameters

increasing length, the fibers have more reach and are able to connect with other fibers more easily. So the number of fibers needed to make the percolation pathway is lesser.

The critical volume fractions follow a power law relation with respect to length. Figure 8, shows a power law fitting for fibers with D=.02 and different lengths.

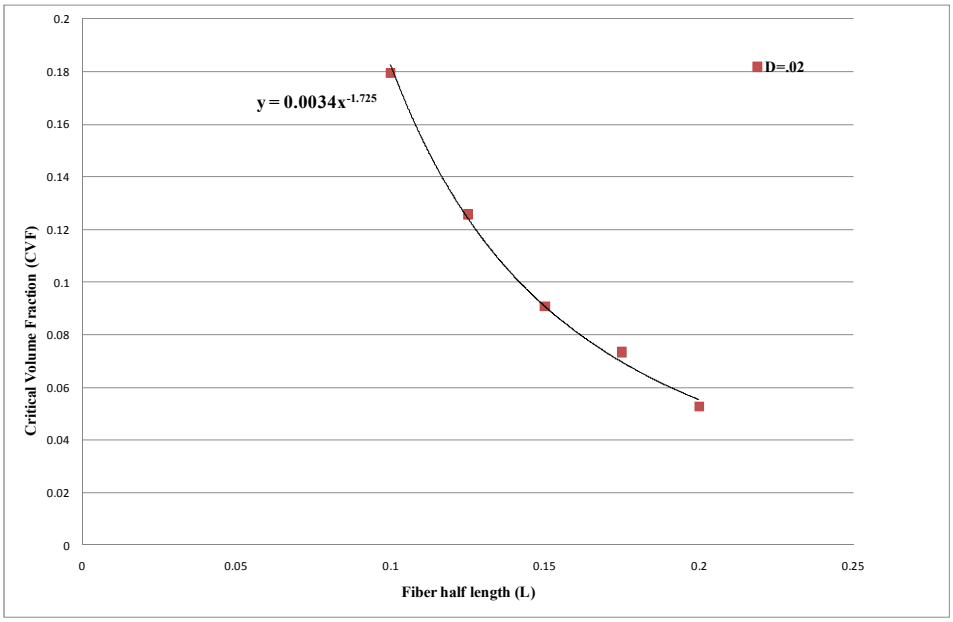

Figure 8 Power law fitting for fiber with D=.02

It can also be observed that for the same length, the critical volume fraction increases with the diameter of the fiber. Table 1 and Table 2 represent the critical fiber numbers and the critical volume fractions for different diameters at L=0.1 and L=0.2 respectively. It can be observed that the critical fiber number decreases as the fiber diameter increases. This is because; the higher diameters enable better connection between the fibers, thus reducing the fibers needed to reach the percolation threshold. On the other hand the CVF increases with increasing diameter. This is because of the dominance of the D^2 term in the expression for the critical volume fraction.

Table 1 Fiber number and CVF at different diameters for L=0.1

D=.005		D=.0125		D=.02	
Fiber#	**CVF**	**Fiber#**	**CVF**	**Fiber#**	**CVF**
8630	0.0339	4790	0.1176	2780	0.1747
9800	0.0385	4720	0.1158	2910	0.1828
10800	0.0424	4810	0.1181	2900	0.1822
10600	0.0416	4590	0.1127	2910	0.1828
10600	0.0416	4770	0.1171	2850	0.1791
10600	0.0416	4700	0.1154	2910	0.1828
8600	0.0338	4900	0.1203	3180	0.1998
10900	0.0428	4690	0.1151	2880	0.181
10700	0.042	4840	0.1188	3010	0.1891
11200	0.044	4620	0.1134	2240	0.1407

Table 2 Fiber number and CVF at different diameters for L=0.2

D=.005		D=.0125		D=.02	
Fiber#	**CVF**	**Fiber#**	**CVF**	**Fiber#**	**CVF**
1300	0.0102	430	0.0211	420	0.0528
1370	0.0108	660	0.0324	310	0.039
1110	0.0087	800	0.0393	370	0.0465
1300	0.0102	570	0.028	540	0.0679
1280	0.0101	710	0.0349	450	0.0565
1150	0.009	720	0.0353	290	0.0364
1220	0.0096	520	0.0255	470	0.0591
1250	0.0098	520	0.0255	410	0.0515
1340	0.0105	650	0.0319	450	0.0565
1070	0.0084	760	0.0373	490	0.0616

The fiber length also plays an important role in determining the number of connections in the percolation cluster. The number of connections in percolation clusters are determined and plotted for different lengths at fixed diameters as shown in Figure 9, Figure 10 and Figure 11.

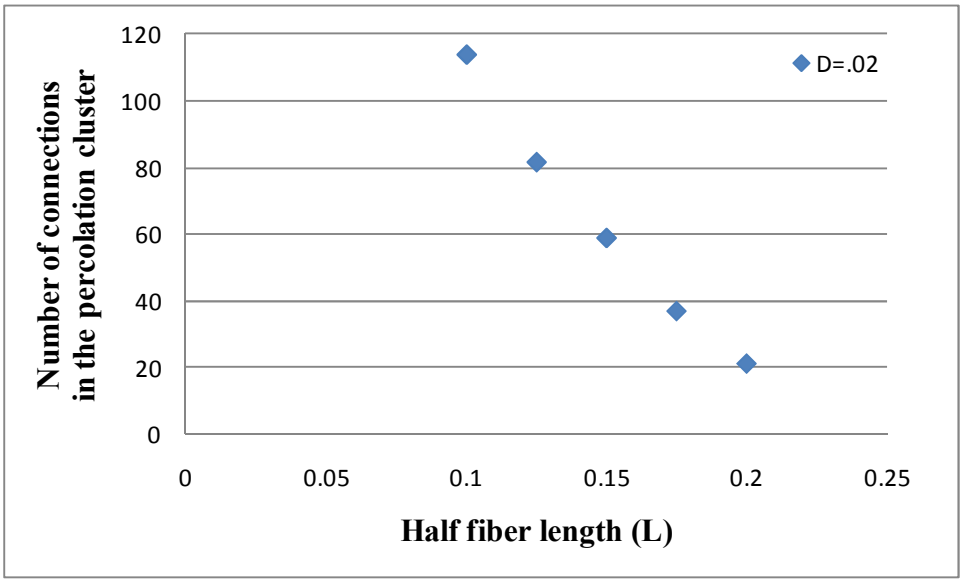

Figure 9 Number of connections in the percolation cluster versus L for D=.02

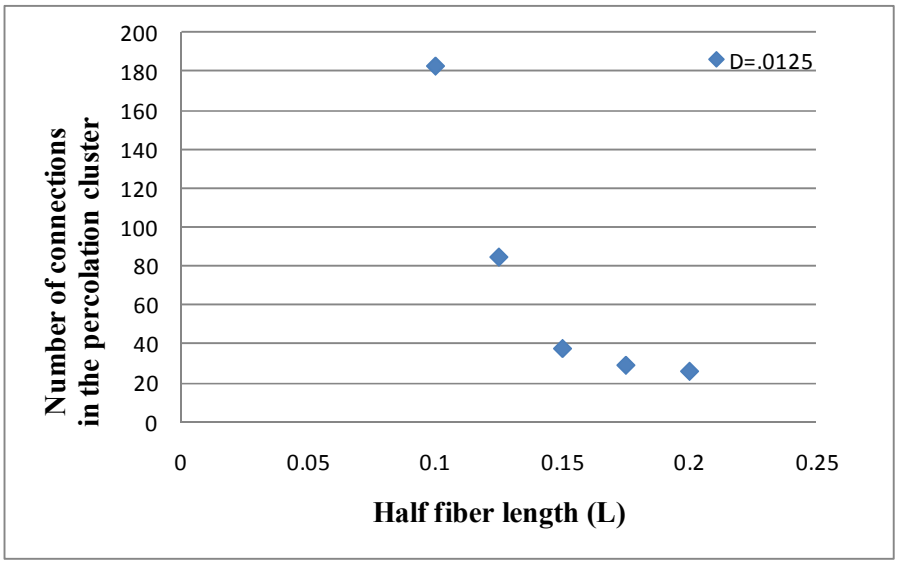

Figure 10 Number of connections in the percolation cluster versus L for D=0.0125

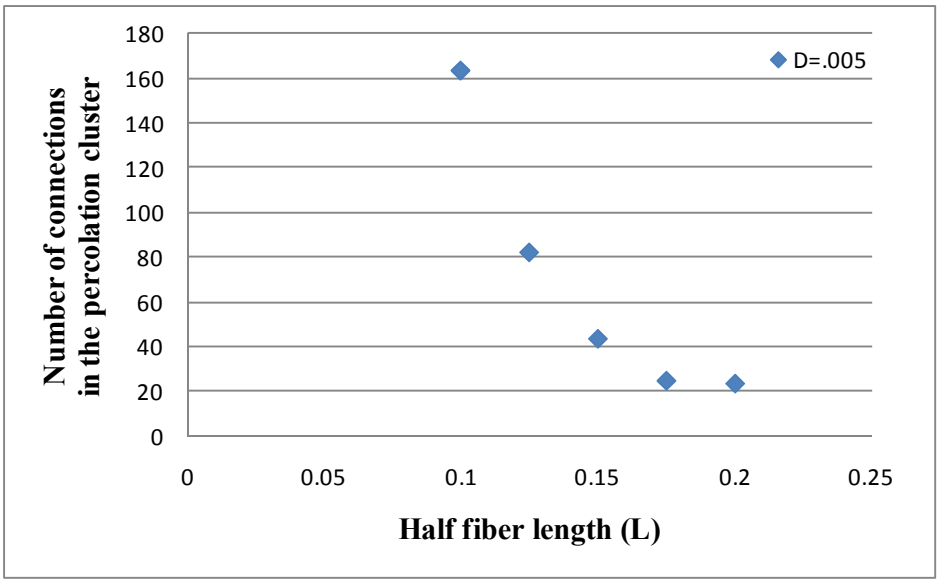

Figure 11 Number of connections in the percolation cluster versus L for D=0.005

For all the diameters considered, the number of connections decreases as the length of the fiber increases. This is because of the lower number of fibers and hence lower fiber connections needed in the pathway to attain percolation.

4.2 Effect of aspect ratio

The aspect ratio 2L/D of the fiber plays an important role in determining the critical volume fraction of the fiber. The CVFs of the fibers are plotted against the aspect ratios by keeping the length fixed in each case as shown in Figure 12.

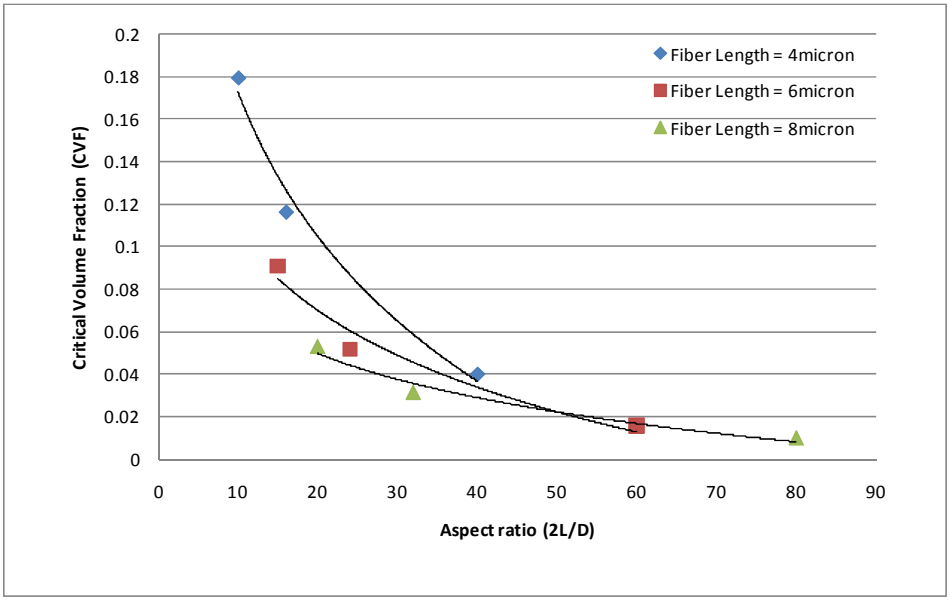

Figure 12 Critical volume fraction versus fiber aspect ratio

The critical volume fraction decreases dramatically with increasing aspect ratio. Since the length is fixed, the critical volume fraction decreases with decreasing diameter.

In the previous section, the CVF was mainly determined by the critical fiber number which tends to change with fiber length. Here, the CVF is dependent on the square of the diameter. So even though the critical fiber number increases with decrease in the diameter due to difficulty in fiber to fiber connection; the decrease in diameter is the dominant factor and influences the CVF to a greater extent. In general, a linear relationship exists between logarithm of critical volume fraction and the logarithm of the aspect ratio.[22] Figure 13 shows the plot between the logarithm of the CVF and the logarithm of the aspect ratio.

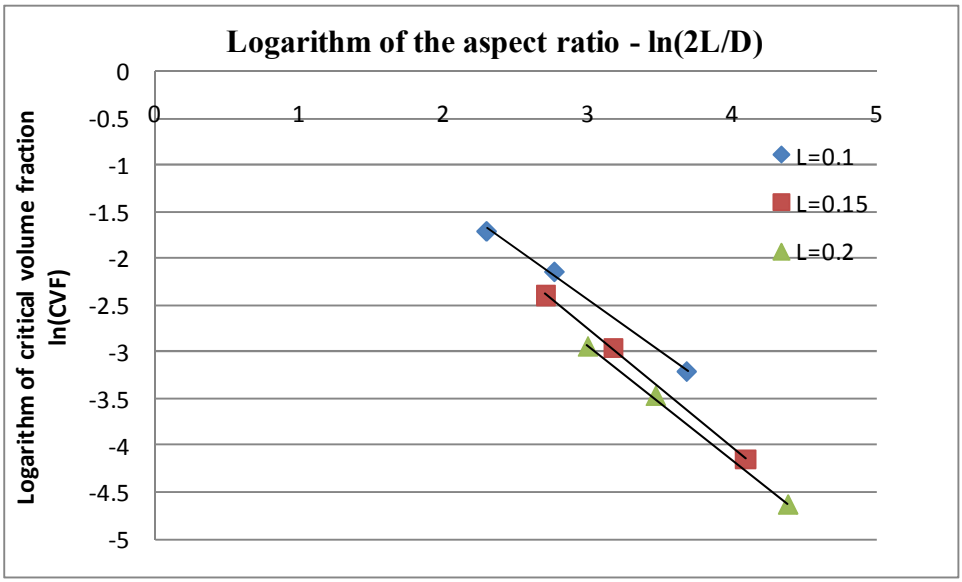

Figure 13 Logarithm of critical volume fraction versus logarithm of the aspect ratio

A linear behavior is observed and the average value of the slope for these three lines is -1.194, which is close to the value obtained by Gao et al.[22] and Foygel et

al.[20] The critical fiber numbers of low aspect ratio fibers are relatively large and it becomes computationally cumbersome to perform these simulations. This is where the linear behavior becomes useful. The linear behavior between the logarithm of the aspect ratio and the logarithm of the critical volume fraction helps to predict the critical volume fractions at low aspect ratios.

4.3 Effect of the matrix

In the simulations and the results discussed above, the fibers were randomly dispersed throughout the volume representing the composite. In reality, this is not the case due to the presence of the matrix phase, which in our case is the polymer part. In the preparation stage of the polymers, usually, there is a solution with the polymers and the fibers. The fibers do not penetrate the particles and during the drying process, the fibers get trapped in the interstitial space between the polymer particles. In order to simulate the effect of the matrix part in the composite, identical cubes were put into the volume representing the composite.

The fibers were placed only in the interstitial space between the cubes. The critical volume fraction of fibers as a function of normalized fiber length for a polymer particle size of 1 micron is shown in Figure 14.

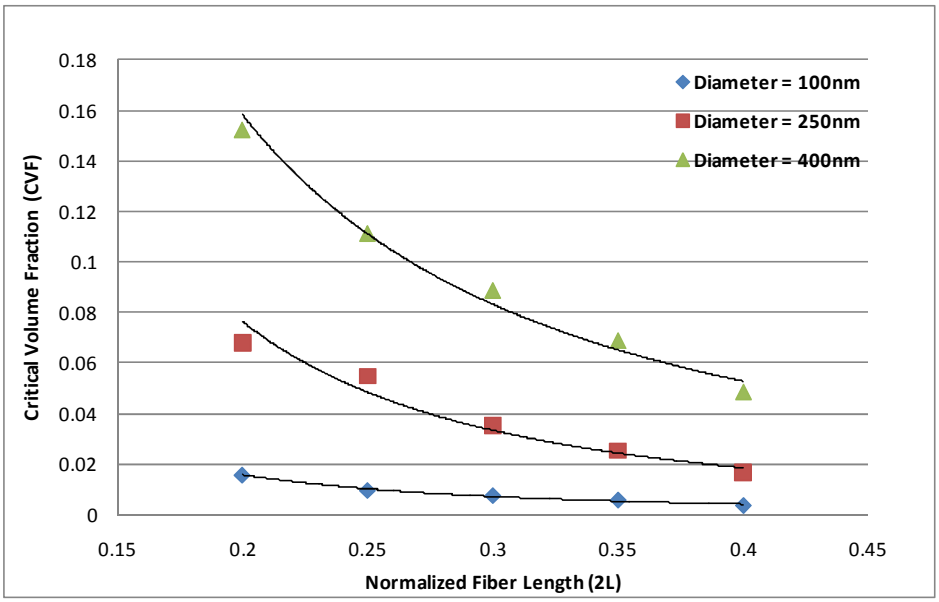

Figure 14 Critical volume fraction versus normalized fiber length for a polymer particles size of 1 micron

The critical volume fractions in Figure 14 are much less than the critical volume fractions in Figure 7 for the same fiber dimensions. This is a predictable result. As the fibers are compressed in the space between the polymers, there is a greater probability for inter-fiber connection. This leads to a lower value of critical volume fraction for the simulations in which the polymer particles are considered. It is also seen that the power law works here as well, to explain the relation between the critical volume fractions and the fiber lengths at a fixed fiber diameter.

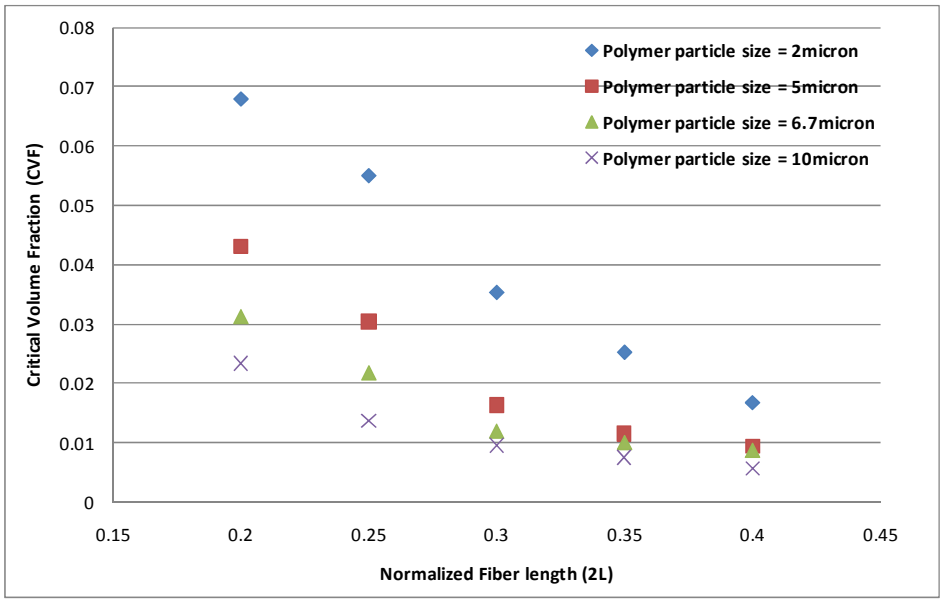

Figure 15 Critical volume faction versus normalized fiber length for different polymer particle (cube) sizes

The critical volume fractions for a fixed fiber diameter of 250nm, when lengths are 4 microns, 5 microns, 6 microns, 7 microns and 8 microns for different polymer particle sizes are shown in Figure 15. The critical volume fractions at a fixed length for all the lengths decrease with increasing particle size. As the volume of the composite is fixed, increasing the particle size results in lower volume available for the fibers to occupy and hence increases their connection probability. This leads to lower volume fractions.

In real composites, the polymer particles are rarely of identical dimensions and the CNTs are highly compacted in the interstitial spaces as seen in the SEM the work of Yu et al.[1]

To make the simulations closer to reality, the polymer particles were modeled as rectangular cuboids as shown in Figure 16 with its edge lengths being generated by random numbers.

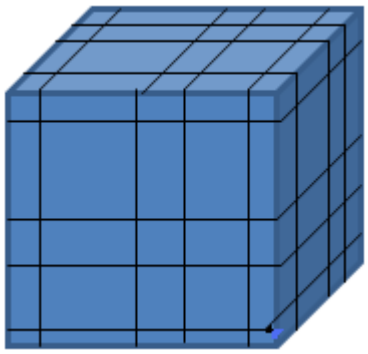

Figure 16 Composite filled with cuboids of different dimensions representing polymer particles

The fibers were placed between intersecting surfaces of any rectangular cuboids. This gives a reliable simulation of the compact packing seen in real composites. Since the model is stepped up closer to reality, real polymer and fiber parameters were incorporated into the simulation. Data and parameters from experimental works of Yu et al. are used for the simulation.[1, 23] In the initial simulations, fiber length was set as 2 microns (L=.05) and the fiber diameter is set to be equal to 10nm (D=.0005). The edge length of a polymer varies from .14 microns to .35 microns following a normal distribution with an average edge length of 650 nm.

In addition to the critical volume fraction, the path length and the number of connections of the percolation cluster are also calculated. The path length is the actual path the electrons travel through the cluster to reach from one end to the other end of the composite to cause electrical conduction. The fibers and path length of a percolation cluster is shown in Figure 17.

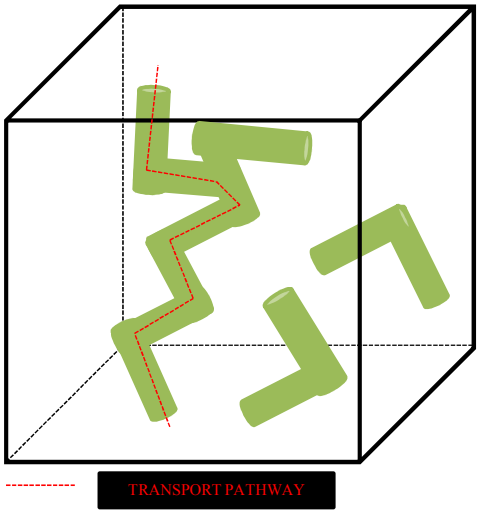

Figure 17 Length of the percolation pathway in the fiber percolation cluster

The percolation pathway has a resistance due to the connections between the fibers and a resistance due to the fibers. These two are considered to be resistances in series. Let n_c be the number of connections in the cluster and let R_c be the unknown resistance to current flow due to fiber connection. Let R_f be the resistance of the fiber pathway.

$$R_f = \rho_f(\frac{l_{fp}}{A_f}) \tag{17}$$

Here, ρ_f, l_{fp} and A_f are the resistivity, path length and the area respectively of the CNT fiber in the composite. The total resistance R_{Total} is given by

$$R_{Total} = R_f + n_c R_c \tag{18}$$

The total resistance of the composite can be found by taking both the path length resistance and the polymer resistance to be in parallel.

$$\frac{1}{R_{Composite}} = \frac{1}{R_{Total}} + \frac{1}{R_{Polymer}} \tag{19}$$

The resistance of the polymer is usually several orders of magnitude higher than the resistance of the fiber path. So in essence, the resistance of the composite is approximately the same as that of the resistance of the fiber path. The electrical conductivity of the sample, σ is obtained as

$$\sigma = \frac{Length_{Composite}}{R_{Total} Area_{Composite}} \tag{20}$$

Here $Length_{Composite}$ and $Area_{Composite}$ are the edge length and face area of the RVE respectively. The expression for the electrical conductivity can be equated to the experimental data to obtain the value of R_c. R_c is taken to be the same for all the connections and it is heavily influenced by factors like degree of connectivity of fibers, the stabilizing agent used in the preparation of the composite and on the polymer used.

Two sets of experimental data matching the parameters of the simulations are available. In the first set, the stabilizer used during the preparation of the composite is

Gum Arabic (GA).[1] In the other experimental data, the stabilizer used during composite preparation is Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS).

The role of GA which acts as the stabilizer in the preparation of the CNT polymer composite is shown in the work of Yu et al. [23] shows. The CNTs are dispersed in water in the form of entangled bundles. The GA attacks the CNTs which are bundled together and separates them by forming a GA coating on the surfaces of the CNTs. This makes the CNTs more uniformly distributed and helps them to get into the interstitial spaces between the polymers more effectively and uniformly.

The role of PEDOT: PSS as a stabilizer in the preparation of CNT polymer composite is also shown in the work of Yu et al.[23]

The stabilizer coating on the fibers has a big impact on the contact resistance between fibers.

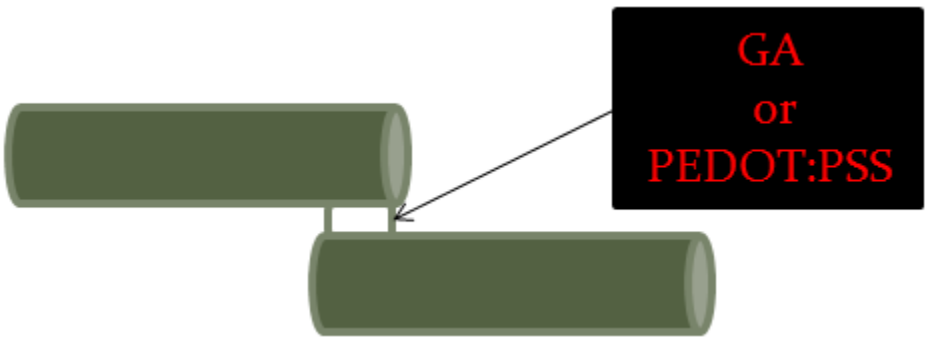

Figure 18 Stabilizer coating between the fibers

Figure 18 shows a schematic of stabilizer coating (GA or PEDOT: PSS) present between two fibers, influencing the contact resistance between. The contact resistance of GA has generally been observed to be greater than the contact resistance of PEDOT: PSS.

Experimental data are used to find the R_c values when the stabilizers used are GA and PEDOT: PSS. R_c value obtained for the case of GA is $1.76\times10^5\,\Omega$. R_c value obtained for the case of PEDOT:PSS is $9.04\times10^2\,\Omega$. R_c values are consistent with values in literature.[24]

Once the value of R_c is found out, R_{Total} and σ for composites with given fiber dimensions, fiber quality and polymer particles can be found through simulations for that particular R_c. CVFs, path lengths and the number of connections in a cluster are found for fiber diameters of 2nm, 10nm, 50nm, 75nm and 100nm; and for fiber lengths of 4 microns, 6 microns, 8 microns and 10 microns. The ratio of the total resistance of the fiber path and the total contact resistance for these different fibers is calculated as R_{ratio}

$$R_{ratio} = R_f / (n_c R_c) \tag{21}$$

R_{ratio} is a very significant quantity. It gives the relative magnitude of fiber and the connection resistance in a composite. It is the factor which decides if the composite is fiber resistance dominated or connection resistance dominated. R_{ratio} of a composite can be varied to change its thermoelectric properties. From the simulation results, R_{ratio} is seen to depend on parameters like the fiber dimensions, type of fiber and the stabilizer

used. R_{ratio} as a function of the critical volume fraction for the different fibers is shown for the case of the two stabilizers GA and PEDOT:PSS in Figure 19 and Figure 20 respectively.

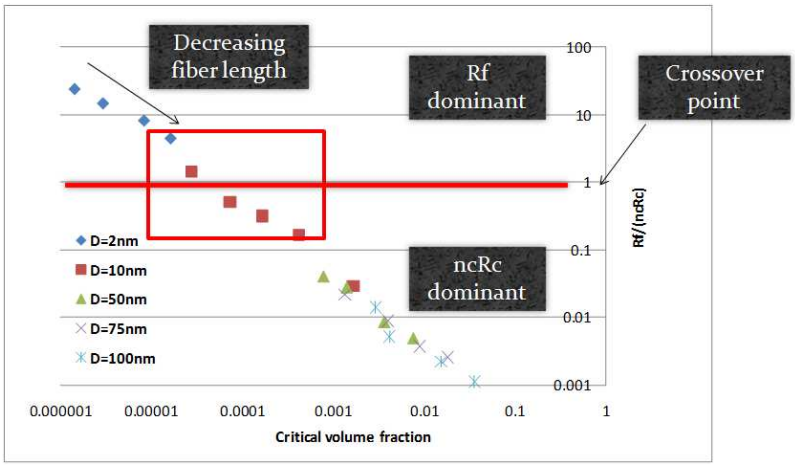

Figure 19 Rf/ncRc versus critical volume fraction for different fiber dimensions when the stabilizer is GA

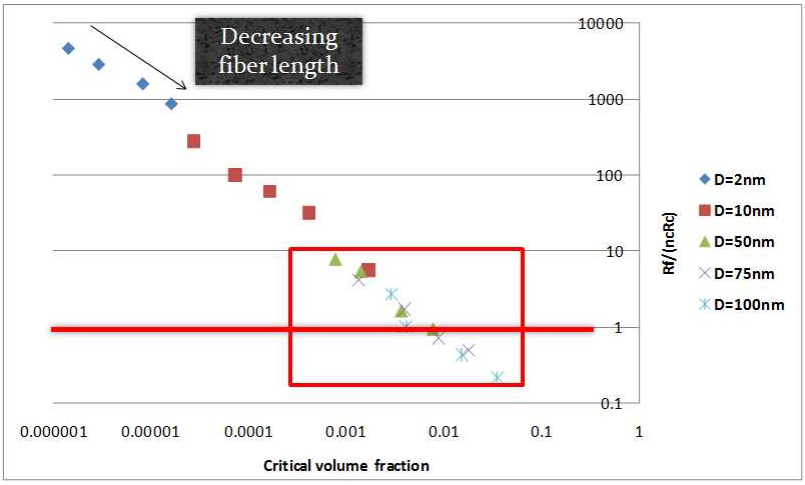

Figure 20 Rf/ncRc versus critical volume fraction for different fiber dimensions when the stabilizer is PEDOT: PSS

In general, it is seen that R_{ratio} decreases with an increase in the critical volume fraction. The critical volume fraction increases along the X-axis due to an increase in diameter and a decrease in the length of the fiber. So, the R_{ratio} in effect decreases because of an increase in diameter and a decrease in length. This seems logical as an increase in the diameter and a decrease in the length causes the numerator of R_{ratio}, that is, R_f to decrease. Decrease in the fiber length leads to an increase in the number of connections. So a decrease in length has an effect of increasing the denominator in the ratio. The figure also depicts the fiber resistance dominated regime and connection resistance dominated regime and the crossover point between the two.

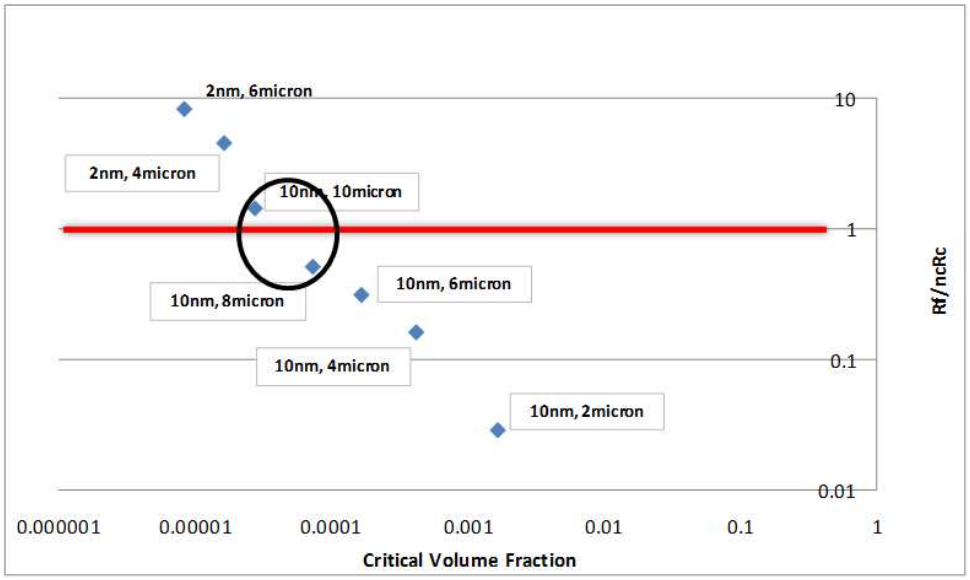

Figure 21 Fiber dimensions near Rf/ncRc=1 with GA as stabilizer

Figure 21 gives the dimensions of the fibers in the composites with GA as the stabilizer which have an R_{ratio} around 1. It is seen that the ratio becomes 1 for a diameter

of 10nm and a length which is in between 8 micron and 10 micron. For instance, if a composite is to be made with R_{ratio}=1, using GA as the stabilizer, CNT fibers having a diameter of 10nm and length between 8micron and 10microns have to be used. For fibers with diameters less than 10nm, the ratio can be made less than or equal to one by decreasing the length of the fiber. As seen in the figure, for fibers with a diameter of 2nm, the length has to be reduced below 4nm to bring the ratio equal to or less than 1. If the length and diameter of the fiber are fixed quantities, for example, for commercially available fibers, then the two ways of changing the ratio are changing the stabilizer or using a fiber with different electrical conductivity. For instance, the fiber with diameter 4 microns and length 2nm, falls in the fiber resistance dominated regime. If the dimensions of this fiber are to be kept constant, then the best way to increase the overall conductivity of the composite would be to change the fiber to highly conductive metallic nanowires etc. as opposed to the use of a different stabilizer which would have a relatively negligible impact. On the other hand, if the fiber that can be used is limited to CNT fibers due to composite property constraints, commercial availability etc.; then the electrical properties can be improved by lowering its length or increasing its diameter.

For a point in the connection resistance dominated regime, for instance fibers with a diameter of 10nm and length 2 micron; if the dimensions of the fiber cannot be changed, the best option would be to use a better stabilizer to bring the ratio closer to one.

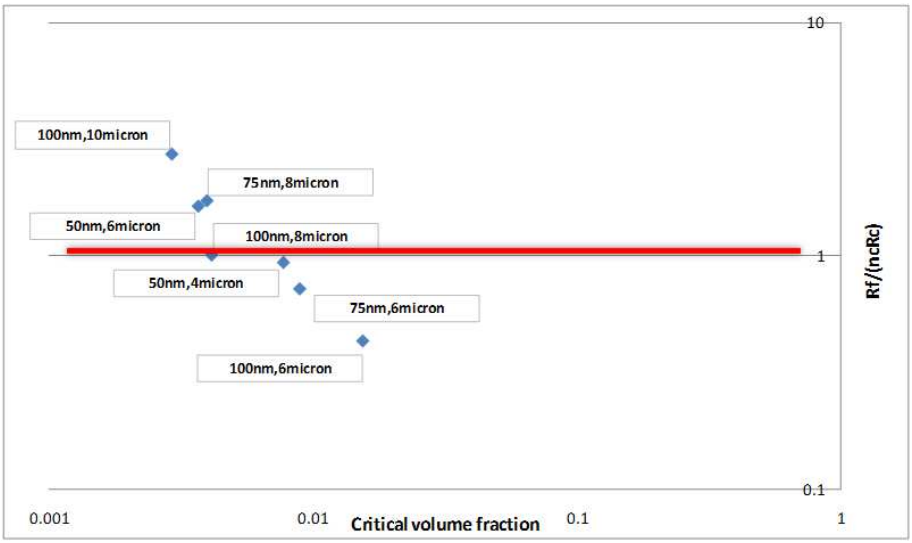

Figure 22 Fiber dimensions near Rf/ncRc=1 with PEDOT: PSS as stabilizer

A similar analysis can be done for the case when PEDOT: PSS is the stabilizer as shown in Figure 22. Since the R_c value is relatively smaller than the case of GA, the dominance of the effect of the stabilizer is small and there is a greater range of fiber dimensions which results in an R_{ratio} close to 1. The ratio becomes 1 in for 50nm diameter for a fiber length in between 4 microns and 6 microns. For 75nm diameter, it becomes 1 for lengths in between 6 microns and 8 microns. For 100nm diameter, the transition happens at approximately 8 microns. It is also interesting to note that the ratio is 1 at higher values of diameters as compared to the case of GA where it was around 10nm. This shows that better conducting fibers, stemming from higher diameters are required to compete with the low junction resistance in the case of PEDOT: PSS.

Here again, for a point with fiber diameter of 100nm and fiber length of 10microns, that is a point in the fiber resistance dominated regime, to increase the

composite conductivity, it would be a good idea to use fibers with lower resistance, if the dimensions cannot be altered. If the dimensions are flexible, the electrical conductivity can be enhanced by decreasing the fiber length or increasing the fiber diameter. On the other hand, for a point in the connection resistance dominated regime, for instance the point with fiber diameter of 100nm and fiber length of 6 microns; the electrical properties can be enhanced more effectively by decreasing the resistance of the stabilizer.

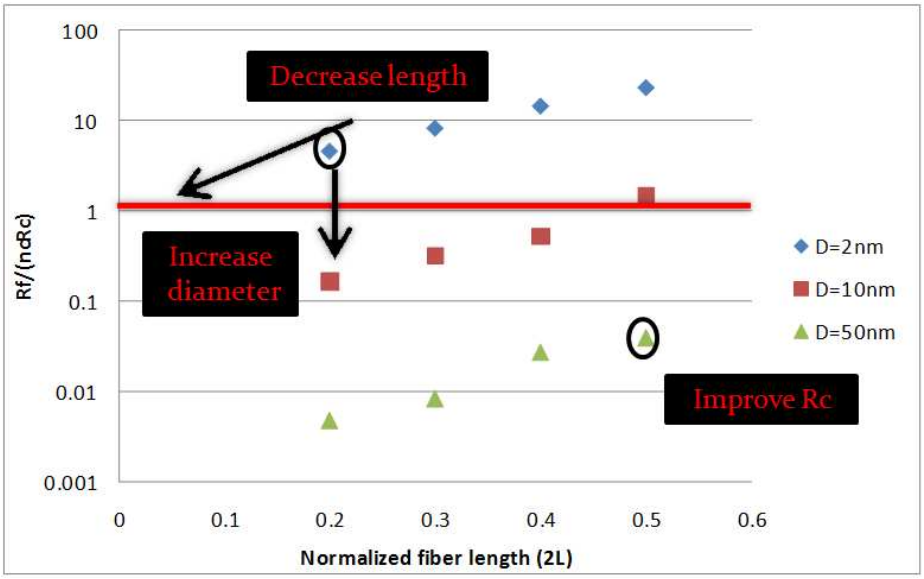

Figure 23 Rf/ncRc for different fiber lengths at fixed diameters for composites with GA as stabilizer

The role of fiber dimensions on the relative effects of fiber resistance and the junction resistance is seen more clearly from Figure 23. For a D=2nm, 2L has to be brought lower than .2 to reach the unity ratio. At the same time, for D=10nm, and 2L=.2 a jump in the ratio below 1 can be made by increasing the fiber diameter or by

improving the electrical conductivity of the fiber. For D=50nm and 2L=.25, it is better to use a stabilizer with lower connection resistance to bring the ratio close to 1. A similar behavior as in Figure 23 is also shown in the case of PEDOT: PSS.

The results obtained here showing the relation between fiber dimensions, type of fiber and the stabilizer used during fiber preparation can prove to be a valuable asset to experimentalists working on, and making polymer fiber composites to modify the properties for different applications. The results can be used by experimentalists as a guide to select design parameters like fiber dimensions, fiber quality and stabilizer to make composites of desired electrical properties.

5. CONCLUSION

A three dimensional model for determining the critical volume fractions and other percolation related parameters for CNT network polymer composites was developed. The effect fiber dimensions like fiber length and fiber aspect ratio on the critical volume fraction was studied. Initially fiber critical volume fractions were investigated for a volume representing the composite containing only the fillers that is the CNT fibers. In the next stage identical cubes representing polymer particles were introduced into the volume. The effect of polymer particle sizes was studied. The polymer particles were in the next stage modified to cuboids to closely represent the actual shape of the polymers and the CNT fibers were distributed in the interstitial spaces between the particles. Simulations were performed using this model and the results were compared with experimental data to obtain the average connection resistance between the fibers for the case two different stabilizers, GA and PEDOT: PSS. These values were utilized to calculate the relative contribution of fiber resistance and the connection resistance to a composite's electrical conductivity. The effect of fiber dimensions, stabilizer used during composite preparation and fiber type were studied systematically and trends were established. These trends are expected to provide valuable information required to tweak electrical properties of composites in experimental studies.

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VITA

Name: Vinay Narayanunni

Address: c/o Dr. Choongho Yu
Department of Mechanical Engineering
Texas A&M University
College Station, TX 77843-3123

Email Address: americain07@neo.tamu.edu

Education: B.Tech., Mechanical Engineering, National Institute of Technology, India, 2007
M.S., Mechanical Engineering, Texas A&M University, 2010