RESEARCH ARTICLE

3D Monte Carlo simulation modeling for the electrical conductivity of carbon nanotube-incorporated polymer nanocomposite using resistance network formation

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Abstract: High electrical and thermal conductivity associated with high stiffness and strength offer tremendous opportunities to the development of a series of carbon nanotube incorporated composite materials for a variety of applications. In particular, a small amount of carbon fibers or carbon nanotubes in a non-conductive polymer will transform a composite into a conductive material, which reveals superb potential of their future application in electronic devices. The relation between the amount of carbon nanotubes in a polymer and the electrical conductivity of it can be studied experimentally as well as theoretically with various simulation models. A three-dimensional (3D) Monte Carlo simulation model using resistance network formation was developed to study the relation between the electrical conductivity of the polymer nanocomposite and the amount of carbon nanotubes dispersed in it. In this model, carbon nanotubes were modeled as curvy cylindrical nanotubes with various lengths and fixed tube diameter, all of which were randomly distributed in a non-conductive constrained volume, which represents polymer. The model can be used to find the volumetric electrical resistance of a constrained cubic structure by forming a comprehensive resistance network among all of the nanotubes in contact. As more and more nanotubes were added into the volume, the electrical conductivity of the volume increases exponentially. However, once the amount of carbon nanotubes reached about 0.1 % vt (volume percentage), electrical percolation was detected, which was consistent with the experimental results. This model can be used to estimate the electrical conductivity of the composite matrix as well as to acquire the electrical percolation threshold.

Keywords: Simulation; Electrical Conductivity; Carbon Nanotube; Polymer Nanocomposite; electrical percolation

1. Introduction

Since its first discovery by Iijima nearly two decades ago[1], carbon nanotube (CNT) has attracted much research and industrial interests because of their unique potentials for multifunctional applications. An exponentially growing number of researchers have since investigated the mechanical and structural properties of CNTs and their strength, stiffness and resilience have been reported to exceed any current material as a consequence of its symmetric structure, which provides great opportunities for the development of new nanocomposite materials. In addition to the exceptional mechanical and structural properties, they also exhibit excellent thermal and electrical characteristics. CNTs are thermally stable up to 2800ºC in vacuum environment and its thermal conductivity is about twice as high as diamond. The electrical conductivity of CNT is close to copper while its electric-current-carrying capacity is a thousand times higher than copper wires[2]. These exceptional properties of CNTs have been utilized in various applications including molecular electronics, field-emission displays, scanning probe microscopy, etc.[3–6].

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Carbon nanotube composites have also attracted a lot of interests because of their unique electrical properties: the dispersion of a very small amount of CNTs leads to a significant improvement in the electrical conductivity of the composite. Therefore, theoretical and experimental studies have been conducted extensively on the effect of the carbon nanotubes to the electrical conductivity of the composite material[7–12].

1.1 Electrical Properties

1.1.1 Electrical Properties of CNT

Because of the availability of the free electrons in this tube-like configuration, CNTs exhibit a considerable electrical characteristics based on the atomic configurations. Some important electronic properties of CNTs are listed on Table 1. Experimental study shows that the multi-walled carbon nanotubes can carry extremely high current densities up to 10^9 - 10^{10} A/cm^2 and can remain stable at high temperature in air for an extensive period of time[13]. The thermal conductivity was also estimated to be an extraordinary high value of 6600 W/Km for an isolated nanotube at room temperature, which is comparable to a diamond or a hypothetical isolated graphene monolayer[14].

Electrical Conductivity	**Metallic or semiconducting**
Electrical Transport	Ballistic, no scattering
Energy Gap (semicond.)	E_g[eV] = 1/d[nm]
Maximum Current Density	~10^{10} A/cm^2
Maximum Strain	0.11% at 1 V
Thermal Conductivity	6600 W/(Km)

Table 1. Important electrical properties of CNTs[11,13,14]

1.1.2 Electrical Properties of CNT-based Polymer Nanocomposite

The high aspect ratio, low density, high conductivity, and extremely high current density of carbon nanotube allows its further application in electronic devices. MWNTs rather than SWNTs have been widely used as conductive materials due to their lower cost, better availability, and easier dispersability. Nevertheless, SWNTs were proved to have even higher intrinsic electrical and thermal conductivity, which enables a further improvement of the properties of the composites. Ounaies *et al.* have studied the electrical conductivities of single wall carbon nanotube reinforced polyimide composites under DC and AC voltages[9]. It shows a dramatic increase in conductivity of the composite with the increased percentage of carbon nanotubes from 0 % vt to 0.1 % vt, but there seems to exist a certain threshold beyond which the increase becomes trivial. Similar phenomena can be observed when an AC voltage was applied to the composite. The electrical conductivity of composite seems to also depend on the frequency of the AC input voltage. The conductivity of the composite with no nanotubes or lower content of nanotubes tends to increase as the frequency increases whereas the frequency seems to have no effect on the composites with high percentage of carbon nanotubes[9]. These results are consistent with the findings by Kim on chemically modified multi-walled carbon nanotube reinforced epoxy composites[16]. Since the polymer is non-conductive, the conductivity of these composites ought to result from the conducting paths formed by the dispersed carbon nanotubes. Therefore, it is possible to estimate and predict the volume conductivity of the composite if the interconnection among the nanotubes are known.

1.2 Modeling of Electrical Conductivity of CNT-based Polymer Nanocomposite

1.2.1 Percolation Threshold Analysis

Percolation theory is analyzed as mathematical problems describing the behavior of connected clusters in a random graph. Due to the similar flowing nature of electrical current, this theory has been widely used to estimate and predict the electrical conductivity of a composite material by assuming the nanotubes as the pathways for electrons[17,18].

As validated experimentally in previous section, when the volume percentage of nanotubes is very low, the conductivity of the composite is very low or even zero depending on the conductivity of the polymer material. However, as the increasing amount of nanotubes, when the volume percentage reaches a critical value, the conductivity starts to rise dramatically. Therefore, there should exist an electrical percolation threshold, above which a stable and continuous conductive path was formed between the two ends. This also explains why the conductivity does not increase much after passing a certain volume percentage of nanotubes because after forming one solid connection between two sides, any additional formation will simply become an extra “wire” in parallel, which will not affect the overall conductivity that much due to extremely high conductivity of carbon nanotubes. Numerous researchers have investigated the electrical percolation threshold of nanocomposite materials in order to understand this phenomena as well as estimate this value for practical manufacturing applications. Parameters including CNT type, atomic structure, morphology, synthesis method, treatment, and polymer type have been taken into account in terms of their effect on the electrical percolation threshold and conductivity of the composite[19–21].

1.2.2 Monte Carlo Method

Monte Carlo method is a class of computational algorithms that estimate the distribution of an unknown probabilistic entity by repeated random sampling. Monte Carlo methods have been widely used in solving physical and mathematical problems when it is very difficult to reach a closed-form expression or impossible to apply a deterministic algorithm. Due to their reliance on repeated computation and repeated random distribution, Monte Carlo methods are often carried out by computers. This method has been used in three major areas: general optimization, numerical simulation, and estimation of a probability distribution. Monte Carlo method is also very useful when investigating systems that involves many degrees of freedom, such as fluids, disordered materials, strongly coupled solids, and cellular structures. Electrical percolation behavior of nanocomposite materials can also be simulated by this method with advanced computational algorithms.

Seager and Pike studied the relationship between percolation and conductivity by applying Monte Carlo techniques to solve many random-lattice percolation models in 2D space. They modeled the composite as straight sticks with equal length and no width dispersed in a constrained area or volume[22,23].

Balberg extended their work to study the reliance of the percolation threshold on the macroscopic anistotropy of systems involving a preferred orientation of the sticks ensemble and the distribution of the stick lengths[24]. He also carried out a 3D Monte Carlo simulation in order to study the percolation behavior of a material consisting of randomly distributed sticks and the effect of the stick aspect ratio and macroscopic anisotropy[25]. Recent studies on the simulation model also include the effects of the tortuosity of nanotubes, tube aspect ratio, tube length, etc. in order to better understand the percolation behavior of the nanocomposite as well as estimate the threshold for nanocomposite manufacturing and practical applications.

1.2.3 Simulation Models

There are hundreds of publications on the electrical percolation threshold and the electrical current of carbon nanotubes in various polymer composite systems. Parameters including nanotube type, synthesis method, treatment, aspect ratio, tortuosity, as well as polymer type and dispersion method were taken into account in order to understand the behavior of the composite. Foygel *et al*. developed a Monte Carlo simulation model to find the percolation threshold of nanotubes dispersed in a low conductive medium[7]. A certain number of spherocylinders of a fixed length and diameter are randomly distributed in a unit cube. The center coordinates and angles of these sticks are randomly generated. The sticks are also assumed to be interpenetratable. As more sticks are added randomly into the cube, it will update the formation of clusters among them and will stop when it detects a complete percolation cluster. For a fixed set of parameters, this procedure was repeated again and again to statistically determine the percolation threshold. This model successfully incorporated Monte Carlo method and the percolation theory approach to extrapolate very low threshold carbon nanotube loads that are needed to substantially increase the conductivity of the polymer nanocomposite. They also concluded that the electrical resistance of the composite is governed by the very high contact resistance between nanotubes when forming a percolation cluster.

However, real carbon nanotubes cannot be perfectly straight as assumed in this model and the curviness of them may affect the properties of the corresponding composite materials substantially including their percolation threshold as well as electrical conductivity. Therefore, a more sophisticated model that includes this characteristics of nanotubes is needed in order to better estimate the electrical behavior. In addition, when two nanotubes interpenetrate or are very close to each other, the equivalent electrical resistance should be calculated based on the contact resistance, and partial tube resistances in parallel or in series.

A more comprehensive model was developed by Dalmas *et al*. to simulate DC electrical conductivity in entangled fibrous networks. Non-straight fibers with high aspect ratio were generated using a spline calculation. The effect of the morphological parameters including aspect ratio and tortuosity as well as the contact electrical resistance on percolation threshold was studied[10].

Carbon nanotubes are synthesized with a very high aspect ratio, which means the length is much greater than the diameter. Therefore, there is a high chance that the carbon nanotubes will form an entangled network within the composite matrix. The study on the impact of their tortuosity and curviness on the percolation and electrical properties is still being conducted and these microstructures have added a lot of complexity to the modeling compared to straight cylinder assumptions. Based on the interconnections between these tubes, the electrical resistance was calculated and added starting from the bottom to the top. Once there is a complete connection from two ends, percolation occurs and the electrical resistance was calculated. If more nanotubes were added after percolation threshold, more clusters will form and the conductivity of the composite will increase dramatically, which is verified with experimental results. When the fraction of nanotubes reaches a certain value, a solid connection of nanotubes were considered to be formed and the electrical resistance of the whole volume simply depends on the resistance of the nanotubes. This is why no huge improvement of conductivity was found by adding more carbon nanotubes after passing this critical fraction. This process was repeated hundreds of times with different distribution profiles of nanotubes with fixed constrained volume. The percolation threshold, critical volume fraction and the electrical resistance at these points can be analyzed to find an equivalent or an average electrical resistance of a composite when a certain fraction of nanotubes are added into a polymer composite.

Compared to the previous model, this model included the curviness of the nanotubes, which may play an important role in the electrical conductivity of the polymer nanocomposite. This model also considered the situations when two fibers are very close to each other, there is an additional contact resistance as well as partial resistance in series and in parallel, which is closer to the real networks formed in a carbon nanotubes/polymer composite. On the other hand, the assumption of non-straight nanotube microstructures will dramatically increase the complexity of the model and consequently require much longer simulation time. However, both models assumed the length, diameter, aspect ratio and the electrical conductivity of the nanotubes to be the same. In real nanocomposite, the electrical conductivity of the carbon nanotube depends on its length, diameter, curviness, and the tortuosity. Therefore, these effects should also be considered when modeling the individual nanotube.

2. Simulation

2.1 Modeling of Nanotubes

Conductive nanotubes are modeled as a curvy fiber connected by a certain number of nodes as shown in Figure 1[10,26]. The diameter of the tube is assumed to be 1 nm and the lengths varying from 5 to 10 µm. Once the lengths of all the tubes are randomly generated within this range, each tube was divided into a number of segments of equal length. A starting point was randomly positioned in a constrained volume. Based on the initial point, the second point was calculated by following Equation 1 below.

$$\begin{bmatrix} X(i+1) \\ Y(i+1) \\ Z(i+1) \end{bmatrix} = \begin{bmatrix} X(i) \\ Y(i) \\ Z(i) \end{bmatrix} + \frac{L}{n} * \begin{bmatrix} sin(\theta)\,cos(\theta) \\ sin(\theta)\,sin(\theta) \\ cos(\theta) \end{bmatrix} \qquad [1]$$

where $[X(i+1), Y(i+1), Z(i+1)]^T$ and $[X(i), Y(i), Z(i)]^T$ are the Cartesian coordinates of the new and previous points, L is the total length of the tube, n is the number of segments, and $[\sin(\theta)\cos(\theta), \sin(\theta)\sin(\theta), \cos(\theta)]^T$ is the directional transformation matrix with θ ranging from 0 to 30 degree. Successive points were created with the same process until the full length of the tube was reached as shown in Figure 1. Now a curvy nanotube fiber was created, which is very similar to the actual morphology of carbon nanotubes. The geometry and morphology of this nanotube model can be easily modified by changing the range of the tube lengths, number of divided segments, and the range of the direction angle. By using the same process, a large number of nanotubes can be created and randomly distributed in a constrained volume as shown in Figure 2.

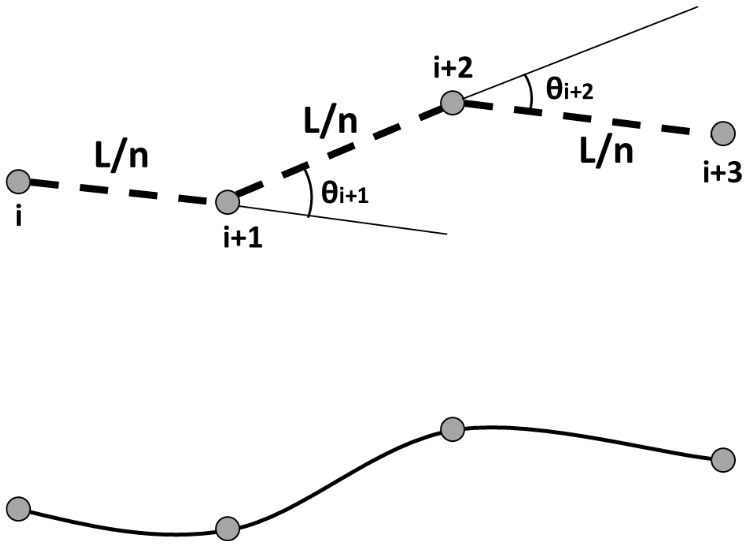

Figure 1. Formation of a curvy nanotube by connecting nodes.

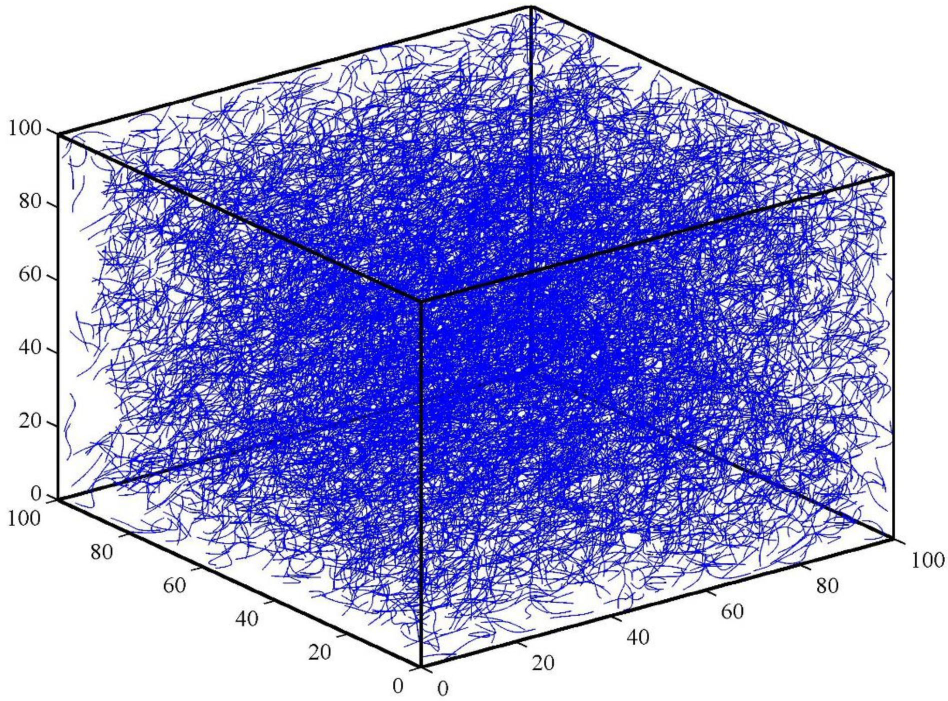

Figure 2. 10000 nanotubes randomly distributed in a constrained volume of 100 ×100 × 100 μm.

2.2 Resistance Network Formation

In order to evaluate the connectivity of nanotubes, the distance among all tubes were calculated by finding the minimum distance between any two tubes. When the distance is less than a certain threshold, for example, 0.01 nm, they are considered to be in contact and a contact resistance was applied between them. The tubes can be either in parallel or in series. An equivalent resistance network can be built based on these connections with one example shown in Figure 3. All the tubes that are in contact with the bottom or the top surface were considered to be connected and were assigned the node number of 0 and 99999, respectively under the assumption that the total number of tubes are less than 100000. Note that if the total number of tubes exceed this number, it can be modified in the simulation model.

There are three types of resistance that need to be considered in this system including tube resistance (~10 kΩ), contact resistance (100 kΩ ~ 3.4 MΩ), and tunneling resistance (1011 ~ 1013 Ω)[7,8,27]. Tube resistance is negligible compared to the other two resistances. Also, the carbon nanotubes are normally wrapped with polymer chains and cannot have a direct contact with each other, which means the tunneling resistance would predominantly determine the total net resistance of the composite system. For the simulation purpose, the minimal distance and the corresponding tunneling resistance were chosen to be 1 nm and 1011 Ω, respectively. These parameters can be easily modified based on the actual properties of the composite material.

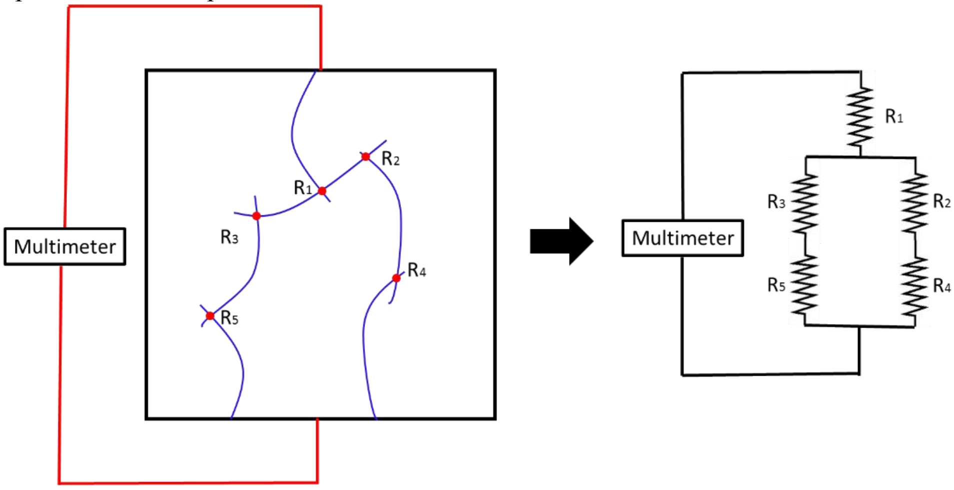

Figure 3. Electrical circuit representation of connections among the tubes.

Once all connections were measured and resistances were applied, a complete resistance network was formed. A SPICE® circuit file was generated based on this information and then loaded into MultiSim® Multimeter as shown in Figure 4. The multimeter would display the total volumetric resistance between the top and bottom.

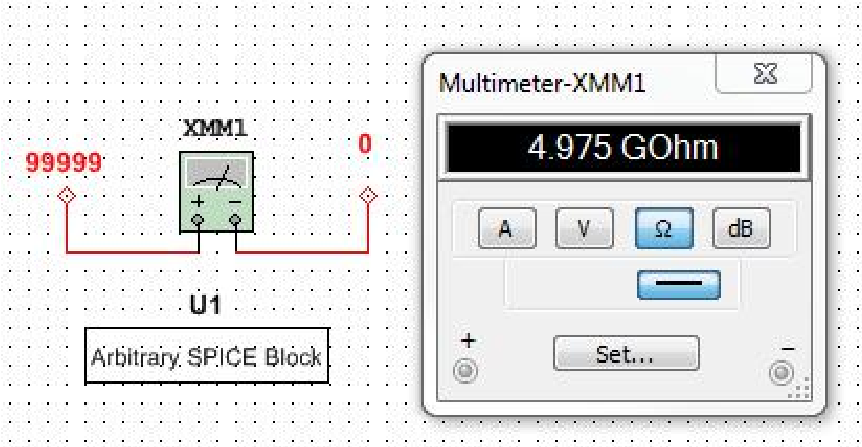

Figure 4. Circuit of the Multimeter in MultiSim® Program to measure the equivalent electrical resistance. Node 0 and 99999 are connected to the top and bottom of the volume, respectively.

3. Results and discussions

The simulation was conducted for four cubical volumes of 50 × 50 × 50 μm, 100 × 100 × 100 μm, 200 × 200 × 200 μm, and 500 × 500 × 500 μm, respectively. Each tube was composed of six nodes being connected to form one curvy line. Note that higher accuracy can be achieved by increasing the number of segments for each nanotube but on the other hand, it will increase the simulation complexity and time dramatically. A predefined number of tubes with fixed tube diameter but various lengths ranging from 5 to 10 μm were randomly dispersed in the volume. Then the electrical resistance between the top and bottom surface was measured. If the resistance is shown as infinity, it means there is no electrical percolation occurred and more tubes were added into the volume.

Figure 5 shows the comparison between the experimental and simulation results on the electrical percolation threshold. As more and more tubes were dispersed into the volume, the electrical conductivity showed an exponential increase, which has also been observed in numerous experimental research. When the amount of nanotubes reached above 0.1 % vt, the electrical conductivity showed a very small increment even when an extensive amount of nanotubes were added into the volume. Therefore, according to this simulation model, 0.1 % vt can be considered as the electrical percolation threshold of the composite system. Once a stable percolation was achieved, more dispersion of nanotubes seemed not to affect the volume conductivity significantly because these additional tubes may form supplementary resistance networks in addition to the pre-established one, which would not yield a dramatic increase in conductivity. This phenomenon has also been observed in numerous experimental results.

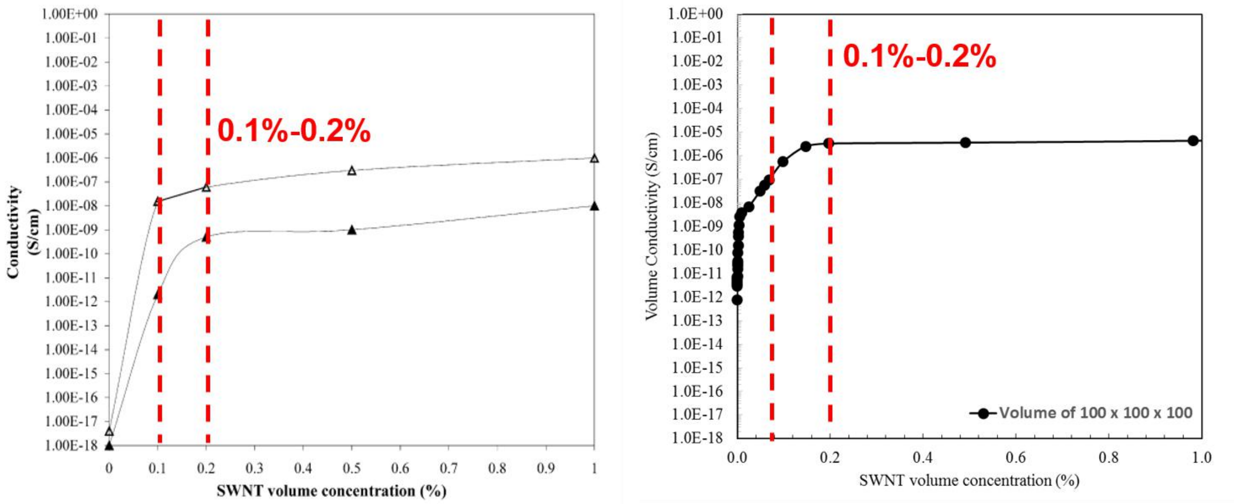

Figure 5. Comparison between experimental (left) and simulational (right) electrical percolation threshold at 0.1% - 0.2 %.

When the volume of the composite is very small, the curvy nanotubes inside tend to form more connections with each other, which yields a higher electrical conductivity as well as a faster reach of the electrical percolation as shown in **Figure 7.** As the volume increases, the length of the nanotubes no longer influences the number of connections among nanotubes and thus a more accurate estimation of the electrical percolation can be expected. Therefore, based on this simulation model, the relation between the electrical conductivity of the composite system and the volume percentage of the carbon nanotubes can be estimated and corroborated with experimental results if the tunneling resistance between tubes, minimal distance threshold, dimension of the composite, and the volume or weight percentage of the nanotubes are known. This model can also be used as a preliminary estimation of the amount of CNTs needed to produce a CNT-based polymer nanocomposite with a desired electrical conductivity or resistance.

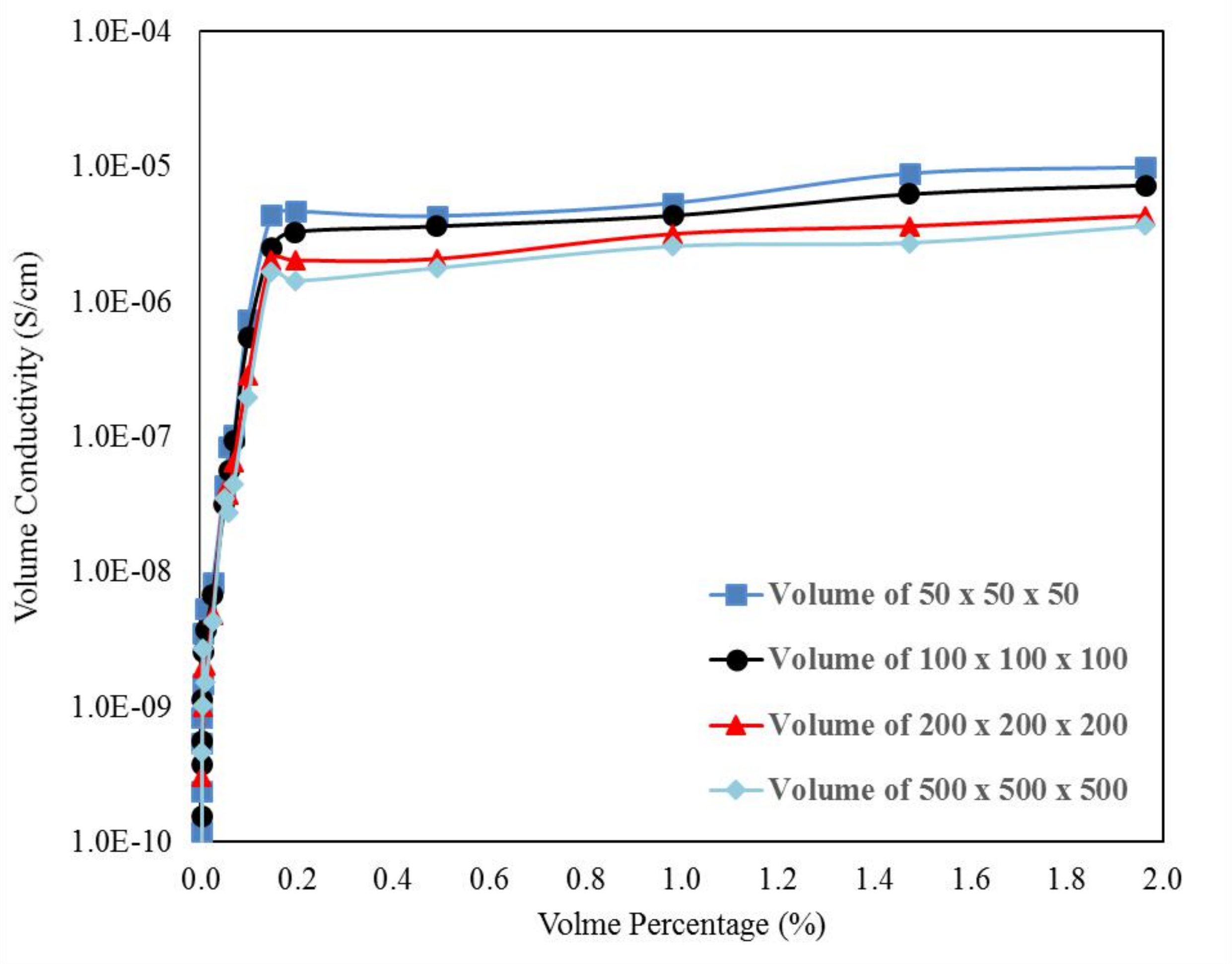

Figure 6. Volume electrical conductivity versus volume percentage of CNTs at different sizes of constrained volumes. Volume lengths are in unit of µm.

4. Conclusions

A 3D Monte Carlo simulation model based on electrical percolation theory was developed to estimate and analyze the relation between the electrical conductivity of the CNT-based polymer nanocomposite and the amount of CNTs in the composite system. The conclusion can be summarized as follows:

Carbon nanotubes were modeled as a curvy fiber composed of a certain number of segments of equal length. The length range of nanotubes can be assigned based on the real composite system.

A Matlab®-based 3D Monte Carlo simulation model was developed to find the minimum distance between any two nanotubes and a cluster file was created for the formation of resistance network.

MultiSim® program was developed to measure the equivalent resistance between the top and bottom surface of the constrained volume.

The electrical percolation threshold of the CNT-based polymer nanocomposite system was found to be about 0.1 % vt, above which, no significant increase in electrical conductivity was observed.

This simulation model can be further improved by considering the tube resistance as a function of length, diameter, curviness, tortuity etc., tunneling or contact resistance as a function of distance among tubes, larger volume of composite, etc. to estimate the electrical effect of the carbon nanotubes to the polymer nanocomposite.

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