Characteristics of the electrical percolation in carbon nanotubes/polymer nanocomposites

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Abstract

We study the onset of electrical percolation in multi-walled carbon nanotubes (MWNTs)/epoxy nanocomposites. Experiments show a threshold value of 3.2 wt% of MWNTs for percolation to occur. Simulations based on two varied approaches are carried out to evaluate the conductivity characteristics resulting from increasing MWNT content. Simple Monte Carlo simulations in which MWNTs are modeled as either 1-dimensional sticks or 2-dimensional narrow rectangles dispersed in a 2-dimensional simulation volume are shown to yield a percolation threshold in close agreement with experiments. We find that a higher degree of anisotropy in the orientation of nanotubes or of the waviness, leads to an increase in the percolation threshold. A more insightful approach encompassing the quantum tunneling effect is also undertaken using the tight-binding simulations. Consideration of the tunneling effect is found to be particularly important when the nanotube aspect ratio is small, the case in which simpler Monte-Carlo simulations over-estimate the percolation threshold.

Introduction

Carbon Nanotubes (CNTs) have remarkable electrical and mechanical properties such as extremely high conductance and Young's modulus.[1–3] Their use in nanocomposites as a filler material can be viewed as one of the most promising area driven towards commercial applications. Of particular interest, are the CNT/polymer composites, since an addition of a small amount of conductive CNTs to an otherwise insulating polymer matrix, results in nanocomposites with highly enhanced electrical conductivity.[4,5] The critical content of CNTs that characterizes a drastic increase in conductivity is commonly termed as the electrical percolation threshold (EPT). Classical percolation theories have been proposed which essentially examine the formation of conductive pathways inside the polymer matrix in the form of uninterrupted clusters of connected CNTs.[6] On the other hand, some other studies also indicate importance of considering quantum effects such as electronic tunneling between neighboring CNTs in order to explain EPT as well as conductivity.[7] The CNT/polymer nanocomposites are thus an alluring avenue for research due in their potential func-

tional applications in optoelectronic devices[8] and organic light emitting diodes.[9]

In order to probe EPT in nanocomposites, many theoretical and numerical studies based on different methods such as continuum mechanics and Monte Carlo simulations have been carried out. In particular, Monte Carlo methods have been extensively used for numerical studies of electrical percolation, formation of percolation networks as well as effects of varying parameters on the threshold.[10–13] With the help of simulations based on simple 2-dimensional (2D) modeling of randomly dispersed fillers, Natsuki *et al.* investigated relation between percolation behavior and orientation as well as the aspect ratio of fillers.[14] In general, exponential decrease in percolation threshold with an increase in aspect ratio is found.[15] For CNT films, Behnam *et al.* also found that the film conductivity depends upon the alignment of nanotubes such that the highest conductivity obtained at partially aligned CNTs.[16] Other studies extending to 3-dimensional (3D) simulations further revealed qualitatively similar features. High aspect ratio nanotubes have been observed to tend to curl up in composites and thus it is important to take into account the effect of waviness. By employing 3D models with randomly distributed curved fibers of finite width, it was found that the critical volume fraction increases with an increase in the degree of waviness,[17] with an accompanying effect of reduction of electrical conductivity.[18] Hu *et al.*also emphasized that poor dispersion of nanotubes in the matrix that can lead to the formation of agglomerates, significantly raises the percolation threshold.[18]

In this paper, we study the electrical properties of MWNT/epoxy resin composites. Conductivity measurements reveal existence of a percolation threshold at 3.2 wt % of MWNTs. Monte Carlo simulations are carried out using simple 2D models for nanocomposites to investigate the effects of nanotube volume fraction, degree of waviness, degree of anisotropy as well as of the aspect ratio in relation to percolation behavior. Further, a refined approach of incorporating quantum effects such as inter-tube tunneling is also implemented via tight binding simulations, which is particularly important for low aspect ratio nanotubes.

The rest of the paper is organized as follows. Next section consists of the details of experimental synthesis of MWNT/epoxy nanocomposites and the results of conductivity measurements.

We then introduce the details of the Monte Carlo simulations and various models studied. Results of the numerical simulations are presented and discussed in the following section. The underlying details of the calculations based on tight-binding model and the respective results are presented in prior to presenting the concluding remarks.

Experimental Details

A commercial EPONTM Resin 828 (epoxy resin) with density of 1.17 g/cm^3 was supplied by Hexion Specially Chemicals, Inc. and high purity ($> 97\%$) multi-walled carbon nanotubes with a density of 2.6 g/cm^3, diameter of 10-30 nm, and length $> 10\mu m$ was supplied by Nanothinx S.A. Using non-covalent functionalization method, the CNTs were sonicated in dimethylformamide/ethanol as a solvent and cured at 120 ^oC for 2 hours. The inset in Figure 1 shows a scanning electron image of CNTs/epoxy resin nanocomposite after curing.

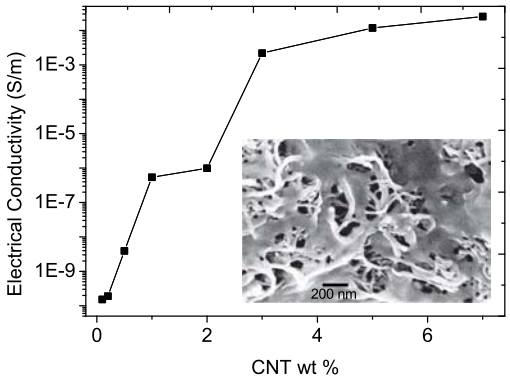

Figure 1: Electrical conductivity of the MWNT/Epoxy resin nanocomposites against the CNT weight percentage. The inset shows a SEM image of the composite.

Electrical conductivity (σ) calculated from the I-V curves (see supplementary material S1) as a function of weight percent of MWNTs is displayed in Figure 1. Conduction can be observed to remain negligible at very small CNT content, which does not allow the formation of conducting channels. The percolation threshold is defined here as the point when the electrical conductivity reaches 0.005 S/m and is found at 3.2 wt% (corresponding volume fraction estimated as 1.39

vol%). We have adopted this definition as the accuracy of conductivity measurement accuracy was poor when MWNT content was less than 1 wt% and even with increasing CNT content the increasing conductivity is comparatively small for direct practical applications of the nanocomposite.

Simulation Methodology

The percolation behavior in CNT-polymer composites is attributable to the high electrical conductivities of CNTs in general. Within a polymer matrix, a continuous channel may get formed by contacts between nanotubes in proximity leading to abrupt enhancements in the electrical conductivity. Formation of CNT networks in a polymer matrix can be modeled simplistically by a 2D simulation cell in which a number of CNTs described as line segments of specified length are dispersed randomly. Each segment can be considered as a 1-dimensional (1D) electrical conductor. Within this highly simplified model, an intersection of two segments can be further considered as a perfect conducting junction with zero contact resistance. It can then be determined whether such interconnections in a simulation cell for a given number of dispersed CNTs can lead to continuous channel formation from one edge of the cell to its opposite one and thereby establish a percolation behavior.

We first consider a 2D simulation cell of size $[1\mu\text{m} \times 1\mu\text{m}]$ in which 100 line segments each of a same certain length are introduced randomly. This case closely represents isotropic distribution of CNTs in a thin film of polymer matrix. Percolation probability is then determined from the formation of a fully connected edge to edge network formation in an ensemble of 100 simulation runs. It is assumed that a percolation probability greater than 0.5 is indicative of an instance of EPT in the system. Percolation probability is obtained as a function of nanotube length, which serves as an indirect measure of volume fraction in 1D cases. To evaluate orientation effects, anisotropy can be introduced in this model by restricting the orientation angle θ of any segment between zero to $\pm\theta_u$. $\theta_u = 0$ represents a fully anisotropic case in which all the segments are aligned in the same direction whereas $\theta_u = 90^\circ$ indicates an isotropic case. For a perfectly isotropic

distribution, percolation is examined for various nanotube lengths in the range of 0.2μm to 0.5μm. For the anisotropic simulations, nanotubes are distributed with an angular dispersion of θ such that $-\theta_u \leq \theta \leq \theta_u$ where θ_u is the maximum angle allowed for the nanobutes. We consider a wide range of θ_u from 5° to 90° while the simulated nanotube length is varied from 0.2 to 0.7 μm.

Further, we account for the common tendency of CNTs to curl up, by treating them as polylines. Each nanotube is described as a polyline consisting of n points (or, nodes), representing (n-1) segments. The coordinates of the endpoints of two sequential segments, (x_1, y_1) and (x_2, y_2) from a given polyline bear the following relation:

$$\begin{aligned} x_2 &= x_1 + (L/N)\cos(\beta), \\ y_2 &= y_1 + (L/N)\sin(\beta), \\ \beta &= \beta_{max}(-1 + 2 \times \text{rand}), \end{aligned} \tag{1}$$

where N is the number of polyline segments for a nanotube, β is the bending angle between adjacent segments, β_{max} is the maximum allowed value of β and rand is random number within [0,1].

A further sophistication of the 1D stick models is to assign them a finite width. For 2D representation, CNTs as modeled as rectangles of length L and width D. In the simulation cell, N number of such rectangles are randomly dispersed. The overlap of two rectangles is allowed and forms the basis of determining contact between them. Within this model, it is possible to calculate the critical volume fraction as well as the weight fraction associated with the percolation threshold.

In all the 1D cases, two nanotubes are assumed to be in contact if there exists at least a pair of intersecting segments (intersecting line segments, for polylines). Point of intersection (x_0, y_0) of one segment (with endpoint coordinates (x_1, y_1) and (x_2, y_2)) with the other (of end-point coordinates (x_3, y_3) and (x_4, y_4)) is first calculated. If x_o lies between x_1 and x_2,and between x_3 and x_4, the two segments intersect each other. Further, each nanotube in the simulation cell is considered as single initial cluster. Starting from the CNTs at the lower edge of the simulation cell, pairwise

comparisons are performed to check for connectivity between the rest of the CNTs with the those from cluster 1. In the event of intersection, the clusters are made to assimilate. The 'propagation' front is iteratively calculated by adding those nanotubes. If upon termination the 'top most' nanotube reaches the upper bound, percolation occurs. For each set of input parameters, the percolation probability ($p = N_P/N_S$) is calculated where N_S is the total number of simulations carried out and N_P is the number of percolation instances.

Results and Discussion: 2D Modeling

From a large number of simulations based on various models in a 2D square cell, we note that the percolation probability in each case increases with an increasing effective volume fraction of CNTs and that a clear indication of a threshold exists. EPT in the current work is defined at the probability equal to 0.5 when averaged over 100 simulation runs. In 1D sticks models of CNTs (whether straight line segments or curved lines), the percolation probability is evaluated against the total length of a single line. In the isotropically distributed configuration of 100 straight line segments each of a certain same length, percolation was observed to occur at a critical length of L = 0.256 μm where as shown in Figure 2.

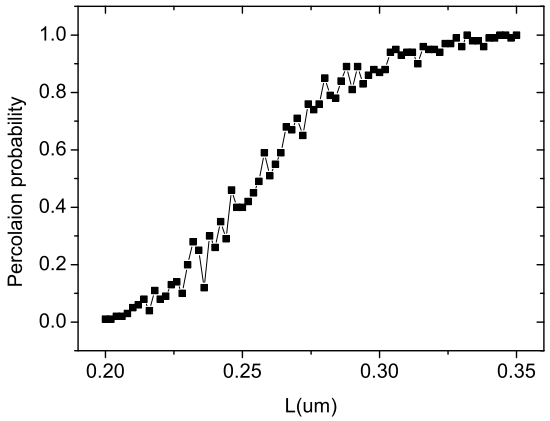

Figure 2: (Probability of percolation in a square simulation cell with 100 isotropically distributed segments each of length L. The percolation threshold defined at probability equal to 0.5 occurs when L = 0.256 μm.

Anisotropy introduced by restricting the alignment of the CNTs in the simulation cell to a

range of angular orientation (θ) shows a significant impact. A small value of θ indicates a high degree of anisotropy while isotropic distribution corresponds to $\theta = 90^{\circ}$. Increase in the degree of anisotropy of CNTs results in a higher percolation threshold, especially when θ is smaller than 45°. As the isotropy increases, the percolation threshold gets stabilized at a comparatively lower value. This result can be comprehended by considering the average number of contacts each CNT makes with others. In a fully anisotropic configuration all the CNTs will be aligned mutually parallel and an end to end percolation will require individual CNT length to be equal to the simulation cell length. With an increasing degree of random orientation, the probability of CNTs intersecting each other becomes larger, thereby making the effective percolation threshold smaller as seen clearly in Figure 3.

Experiments and simulations specifically focussed on orientation effects of CNTs on the drain current in nanobundle thin-film transistors have been studied Pimparkar *et al.*[19] It was found that perfectly aligned tubes yield a higher drain current only when the tube lengths exceed the channel length. For short CNTs on the other hand, where the formation of a percolation network is needed, the optimal percolation threshold was found for perfectly random CNT network, well in agreement with our simulation results. Similar observations of higher conductivity measured in non-aligned SWNT/poly(methyl methacrylate) composites have been reported by Du *et al.*[20,21] Recently, Abbasi *et al.* also reported significant increase in EPT associated with random dispersion of nanotubes in MWNT/polycarbonate nanocomposites.[22]

Usually in the preparation of the nanocomposites, uniform distribution of CNTs within the matrix is desired. In the process, the CNTs get embedded in the matrix, not as straight fillers, but as wavy or tangled wires. In considering the formation of a percolation network, the waviness is highly important, since even for a very large aspect ratio CNT, high degree of waviness renders its effective length smaller (along the percolation direction). We incorporated the waviness of CNTs by treating them as polylines. Each CNT is composed of $(n-1)$ equally long segments which randomly differ in angular orientations. It is clear from Figure 4 that the larger the n, the higher the degree of curvature and the percolation threshold increases significantly. Similar trend has

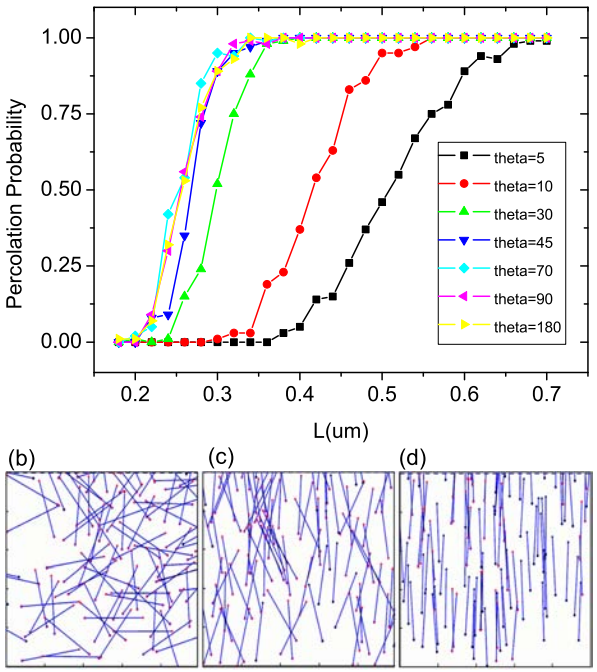

Figure 3: (a) Percolation probability of as a function of length for different angular distribution of 100 CNTs within the simulation cell. (b)-(d) show typical distributions of CNTs when the anisotropic angle is 90°, 30° and 5° respectively.

also been noted in various other theoretical studied using a variety of simulation techniques.[13,18,23] Even though the curled up tubes are also uniformly distributed in a similar manner as the isotropically distributed straight CNTs, due to their bent structure, their effective lengths become shorter leading to a higher EPT.

Instead of using a simple 1D stick model, the finite width of the CNTs may be accounted for in simulations by modeling them as thin rectangles. The influence of aspect ratio (L/D) on the percolation threshold is important and somewhat ambiguous. Our simulation results using 100 CNTs reveal that the percolation behavior in terms of critical length remains mostly unaltered if the aspect ratio is higher than 100. Figure 5 demonstrates that when the aspect ratio is 100 or 1000, the percolation probability is virtually identical and is slightly higher than if the aspect ratio is 10. On the other hand, this trend indicates that the critical volume fraction corresponding to the percolation threshold decreases monotonically with increasing aspect ratio. When the aspect ratio is small, EPT increases since in order to form a conducting percolation network more number of

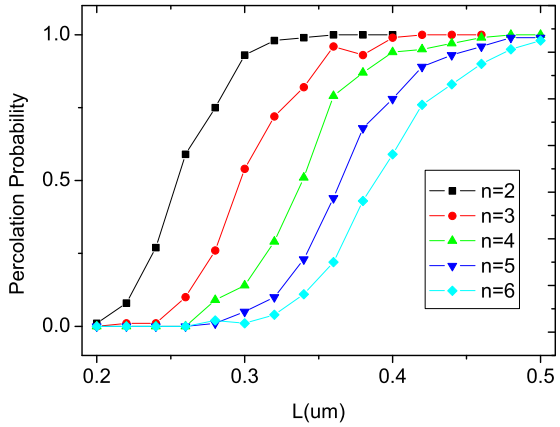

Figure 4: Percolation probability of as a function of total CNT length with differing degrees of waviness. For each curve, (n-1) denotes the number of line segments that make up a single CNT. Higher degree of waviness leads to curling up effect that can be seen reflected in increased percolation threshold.

tubes are required to make sufficient connection points. At $L/D = 100$, we find that the percolation threshold is obtained at 0.62 vol %. This result is in fair agreement with the value of 0.61 vol % in previous reports by Hu *et al.*[18] and Lu *et al.*[15] by using 3D percolation models.

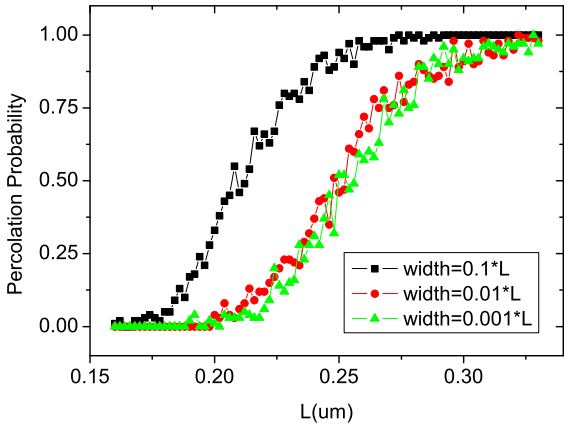

Figure 5: For CNTs modeled as 2D rectangles, percolation probability as a function of length for aspect ratio of 10, 100 and 1000. Invariance in the percolation properties can be observed for CNTs with aspect ratio larger than 100.

For the case of 2D nanotubes EPT in terms of weight percentage can be calculated in a straightforward manner as

$$wt\% = \frac{\rho_{CNT} \times V_{CNT}}{\rho_{CNT} \times V_{CNT} + \rho_{poly} \times V_{poly}} \tag{2}$$

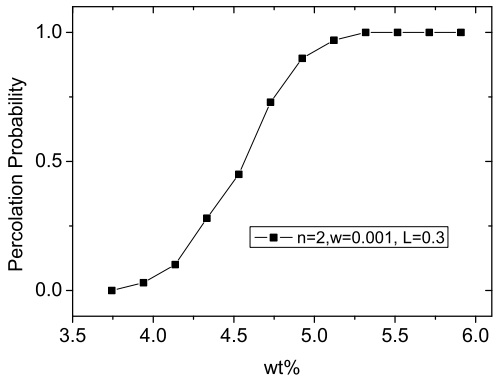

Figure 6: Percolation probability against the CNT weight percentage in a 2D simulation cell with nanotubes treated as narrow-width rectangles.

where ρ_{CNT} and ρ_{poly} are the densities of CNTs and polymer, respectively. Volume occupied by CNTs (V_{CNT}) is calculated from the total number of CNTs and the dimensions of rectangles. On the other hand, polymer volume (V_{poly}) is calculated as V_{CNT} subtracted from the area of 2D simulation cell. Based on the experimental data, ρ_{CNT} and ρ_{poly} are set to be 2.6 g/cm^3 and 1.17 g/cm^3, respectively. Figure 6 shows the results of simulations for CNTs at an aspect ratio of 300, which is expected to be roughly the lower bound for the average aspect ratio of MWNTs used in the actual experiments. The calculated percolation threshold is about 4.5 wt% and is fairly close to the corresponding value measured in experiments. Considering that the experimental MWNTs do not show a fixed aspect ratio due to distribution in their diameters, and that their lengths are expected to be much larger than 10 μm, the small deviation of the simulation results can be easily reconciled. It is thus shown that even a simplified model of 2D sticks to represent nanotubes from the composite is sufficiently appropriate to obtain good agreement with experimental results.

π- Tight Binding (TB) model to account for the quantum tunneling effect

Although the 2D model is successful to account for experimentally observed percolation threshold, it is important to ponder on the validity of dispersion and intersection criteria for nanotubes

in the simulation volume. Physical contact of any two nanotubes in fact implies that that they are still separated from each other by a small distance dictated by van der Waals interactions. As a result, a direct overlap of line segments or of rectangles can be questioned for its validity. When the CNT aspect ratio being considered is very large, such a direct overlap is reasonable. However, in an otherwise case, it becomes important to take into account the non-penetrating configuration of CNTs. A commonly adopted approach in this direction involves the 'excluded volume' concept which prevents interpenetration of nanotubes and a suitably modified connectivity criterion as well as consideration of the electronic tunneling effect. With individual CNTs considered as conductors, charge conduction between two such contacting CNTs may be considered to occur only by the quantum tunneling of electrons. An accurate model of CNT network to study the percolation behavior should thus incorporate quantum effects. Pursuing a more accurate way in this work, we thus consider a π-tight binding (TB) model of non-penetrating CNTs distributed within a simulation cell to study network formation and its electrical percolation behavior.

We utilize the 'Intermolecular Hückel model' to formulate effective hopping matrix element for weakly interacting π system, which is represented as the relative strength of the π-π interaction. The working formula for intermolecular hopping for $ab-initio$ calculation is:

$$H_{ij} = S_{ij}\cos(\omega)[a - b(\cos 2\vartheta + \cos 2\phi) + c\cos 2\vartheta \cos 2\phi] \tag{3}$$

where a, b and c are chosen to provide an optimal agreement between the the conductance of two parallel aligned semi-infinite CNT pairs. Instead of using an exponential decay function to describe π-π binding strength, S_{ij} is calculated by the overlap integral of two separated carbon atoms with only $\pi-$orbital integral being considered in our calculations. $ab-initio$ calculations were performed to evaluate optimum conditions for transmission coefficient as a function of relative separation.

The simulation cell (of size 5 nm $\times$5 nm $\times$7 nm) consists of non-penetrating CNTs of a certain same length. The radius of (4,4) nanotube is 2.7120 Å and the length of its unit cell consisting

of 8 atoms is 1.2297 Å. The number of circumferential carbon rings for a CNT is varied from 10 to 50, corresponding to the length to diameter ratio (L/D) of 2 to 12. Individual (4,4) CNTs are considered to show coherent transport and while the overall conductivity in their agglomeration will be determined by the node tunneling effect between CNT pairs.

Coherent conductance across the device is then calculated within the Landauer-Büttiker formalism as

$$G = (2e^2/h) \int \bar{T}(E) f(E - E_f) dE \tag{4}$$

where $\bar{T}$ is the total transmission from one boundary of the simulation cell to the other. As the actual current flow is not considered in this context, the conductance calculated thus represents the capability of an injected electron at one boundary to travel to the other. It is thus closely associated with the determination of classical percolation.

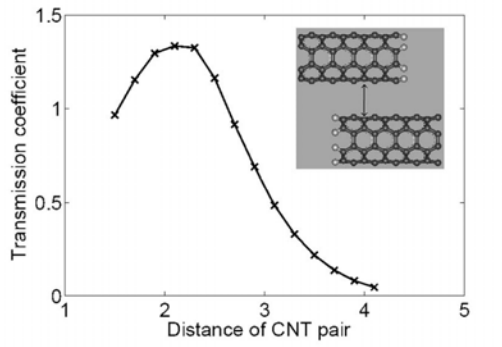

Figure 7: The transmission coefficient versus the distance of the two aligned tubes (Å). The structure for calculating the conductance between two aligned nanotubes is shown in the inset. Conversion from transmission coefficient to conductance may be obtained by multiplying with $2e^2/h$.

A schematic of two parallel (4,4) CNTs separated by a distance d and with one of their ends terminated with hydrogen is shown in the inset of Figure 7. Figure 7 shows the calculated inter-tube conductance versus the separation distance. Maximum conductance occurs when d = 2.5 Å. If the CNTs in a pair are too close, the π-binding may form a sp^3 hybridization and electrons on the CNT surface may get localized resulting in decreased conductance. At a larger separation, conductance may decrease because the potential barrier becomes wider diminishing the tunneling probability.

We studied the percolation network formation in the simulation cell as a function of number of CNTs (effectively, the volume fraction of CNTs) as well as the length dependance of the observed percolation behavior. In Figure 8, a typical plot of nanocomposite conductivity as a function of nanotube volume fraction (VF) is shown for CNTs with 20 circumferential rings. It is interesting to see that conductance increases in steps. The first increase takes place at VF = 0.065% indicating an initial build up of a conductance network. A drastic second boost in conductance can be noted when VF = 0.095%. The dramatic increase in the conductance results from the formation of large number of percolation channels that can easily form when the number of CNTs increases. However, it can be readily noticed that the obtained value of EPT is much smaller as compared that obtained from Monte Carlo simulations at similar aspect ratio. This emphasizes the significance of consideration of quantum tunneling effects at small aspect ratios. Due to the small size of the simulation cell, the maximum number of CNTs that can be distributed in it without penetrating is limited. Such an extreme indicates saturation of nanotubes in the system. In addition, we have also studied the percolation behavior of the nanocomposite for varying lengths of the nanotubes. Nanocomposites with short nanotubes show higher percolation threshold. However, beyond a certain length of the tubes, the threshold remains fairly constant. Longer nanotubes offer a longer segment in a perceived percolation channel for the conduction thereby requiring fewer number of connections with other CNTs in forming it. When the length is small, formation of an uninterrupted network thus necessitates a higher volume fraction.

Conclusions

We have investigated the phenomenon of electrical percolation in CNT/polymer nanocomposites. Conductivity measurements on MWNT/Epoxy composites yield a percolation threshold of 3.2 wt%. We have performed 2D Monte Carlo simulations with CNTs modeled either as 1D sticks or 2D strips. The simulation results demonstrate a clear dependence of EPT on the volume fractions (and thus, weight percentage), the degree of anisotropy, CNT lengths and the degree of wavi-

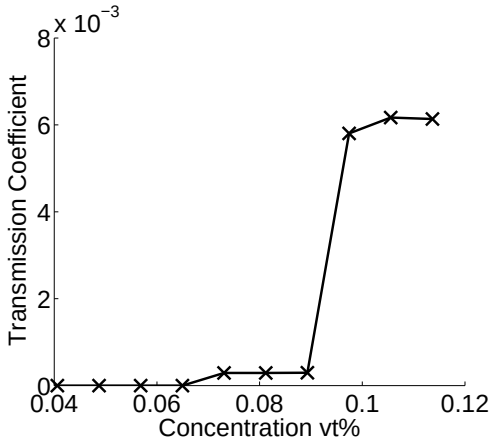

Figure 8: For a dispersion of (4,4) nanotubes each with 20 circumferential carbon-rings, the calculated transmission coefficient against volume percent of CNTs.

ness. For a fixed number of CNT sticks, an increase in their lengths or a decrease in the degree of anisotropy in their dispersion leads to a corresponding increase in the percolation probability, thereby lowering the EPT. Effects of anisotropy are particularly dominant when its degree is very high. Furthermore, the simple 2D model has been shown to yield a value of EPT (4.5 wt %) in reasonable agreement with the experimental observations.

In addition to the simpler Monte-Carlo simulations, which do not explicitly take into account important considerations such as the CNT conductivities, the contact resistance as well as the tunneling effects, we have carried out more sophisticated tight-binding calculations. Inclusion of the tunneling effects is rendered essential in the lowered percolation threshold of 0.095 % (volume fraction) for nanotubes with a small aspect ratio. The current work is hoped to bear significance towards understanding the electrical percolation phenomenon in nanocomposites by putting to use the methods of varying complexity as demanded by considerations of particular problem conditions.

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Supporting Information Available

Details of conductivity measurements and the measured I-V characteristics are presented. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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