Determinant role of tunneling resistance in electrical conductivity of polymer composites reinforced by well dispersed carbon nanotubes

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Three-dimensional Monte Carlo simulation is used to investigate the electrical conductivity of nanocomposites composing of conducting nanofillers and insulating polymer matrix. When nanofillers concentrations low and they are well dispersed in the insulating matrix, electron tunneling resistance between the nanofiller junctions is found to play the dominant role in electron transport. In addition to the tunneling resistance, there is also the resistance of the conducting nanotube segments. These two types of resistance form the resistor network for electron conductance. For composites with well dispersion, individual tubes are separated by polymer molecules and the resulted tunneling resistance can be several orders larger in magnitude than the resistance of individual tubes. Considering the two types of resistors are always linked in an alternating order in the resistor network, the much larger tunneling resistance plays the determinant role in the electrical resistance of nanocomposites. When the contribution of the intrinsic tube resistance is ignored, the number of resistors in conduction paths can be reduced by more than a half and as a result, the computation efficiency is significantly improved. With improved computation efficiency, three-dimensional cubic representative volume elements with high nanotube aspect ratios up to 1000 can be simulated. Simulation results are in good agreement with the critical behaviors predicted by the classical percolation theory, as well as the reported experimental measurements.


I. INTRODUCTION

Due to their superior electrical and mechanical characteristics, carbon nanotubes (CNTs) based composites have attracted extensive interests from both science and engineering communities.1,2 The estimation of the electrical conductivity of these nanocomposites by analytic analysis is very challenging because of the complexity in quantifying the shape, orientation distribution, and electrical properties of nanotubes in composites. A more practical approach to the problem is using numerical simulation to specify distribution and orientations of nanofillers. However, simulations of the electrical conductivity of composites containing tubes of high aspect ratio are computationally intensive and as a result, the simulations are limited to either two-dimensional representative volume elements (RVEs) with high nanofiller aspect ratios or three dimensional (3D) RVEs with low nanofiller aspect ratios far below those of CNTs.3–8 Therefore, the improvement of the efficiency is essential for the application of Monte Carlo methods in studying the electrical conductivity of nanocomposites. In this paper, we proposed a modified simulation methods with improved computation efficiency based on the examination of the determinant role of tunneling resistance in electrical conduction and the unique network structure so that 3D RVEs with high aspect ratios can be simulated. The simulation results were compared to the predictions of classical percolation theory and recent experimental measurements.

In order to calculate the conductivity of composites, the electrical properties of CNTs have to be quantified. In recent years, extensive efforts have been devoted to investigate the electrical properties of individual single walled CNTs (SWCNTs) and the contact resistance across a CNT-CNT junction.9–11 The resistivity of SWCNT shows a strong dependency on chirality and structural defects, and both metallic and semiconducting like transport behaviors have been observed. Ebbesen et al.9 reported the SWCNT resistivity to vary from $5.1 \times 10^{-8}$ to $5.8 \times 10^{-2}$ $\Omega \cdot m$. On the other hand, studies10,11 revealed that the resistance across the CNT-CNT contacts not only depends on the types of constituent CNTs but also has a strong dependence on the external force applied to the contact with a upper limit around $10^{6}$ $\Omega$. In common nanocomposites which usually contain nanotubes of very low concentrations, direct nanotube-nanotube contacts are not likely if the bundling effect is not taken into consideration. Thus, the electron tunneling becomes the major mechanism of electrical conduction through junctions.

II. ELECTRICAL CONDUCTIVITY SIMULATION METHOD

In most of the composite simulations,3–8 a soft core model is employed to allow the overlap among nanotubes and each CNT is represented by its axis (i.e., a line segment) in a cubic RVE. The soft core model apparently contradicts the physical principle that tubes can never penetrate through each other. On the other hand, the hard core model does not have the above mentioned contradiction, yet its implicit assumption of the tube to be infinitely stiff leads to high rejection rates of the generation of tubes during the simulation. In
realistically, the tubes with high aspect ratios can be easily bent at junctions to avoid penetrating each other. Based on these considerations, soft core model is used in current Monte Carlo simulation with the expectation that CNTs bend at the junctions. This approach can produce very reliable predictions of the electrical conduction percolation threshold of systems of sticks, especially with high aspect ratios such as nanofibers and nanotubes.

In this paper, the position and the orientation of CNTs are assumed to follow the uniformly random distribution. Tubes are assumed to be identical in shape and size as shown in Fig. 1. The number of nanotubes is based on the prescribed volume fraction of nanotubes.

In order to represent a composite, periodic boundary condition in all three directions was applied after the generation of a RVE. Fragments of nanotubes outside boundaries of the RVE are cut and then moved back into RVE through opposite face. If a fragment still intersects the RVE boundaries, same operation is applied to it again until all the fragments are inside the RVE.

After applying the periodic boundary condition, an effective resistors network is constructed. To quantify individual resistors, the shortest distance between two tube axis (indexed by 1 and 2) is determined (Fig. 2). For two separated segments AB and EF, a line MN perpendicular to both segments is first determined. Then a perpendicular plane IJKL containing the segment AB is constructed. Line segment EF is then projected onto plane IJKL as E’F’.

When the separation between two axis is smaller than a critical value (in this paper, taken as the diameter of tubes), a junction resistor (i.e., a tunneling resistor) is generated between the two nodes C and G which together define the shortest distance [Fig. 3(a)]. These nodes with the ends (A, B, E, and F) divide the nanotube axis into segments which are represented by filler resistors (i.e., tube resistors). By applying the procedure on each pair of the nanotube axes, an effective resistor network can be established to consist of the junction resistors and the filler segment resistors [Fig. 3(b)]. When the resistance of tubes is ignored in the simulation, only a junction resistor is connected between tube 1 and 2 [Fig. 3(c)].

After the resistor network is constructed, the software WINSPICE is then utilized to calculate the resistance in between the two opposite faces of a RVE. Given the RVE dimensions, the resistance was converted to resistivity.

The main purpose of this paper is to justify the improvement of the simulation efficiency by ignoring the intrinsic resistance of nanotubes based on the fact that the tunneling resistance plays an important role in determining the electrical conductivity of nanocomposites containing dispersed nanotubes. Therefore, only one simulation is performed to obtain...
a single data point. It is expected that the statistic fluctuation of these data points is small because of the large number of nanotubes in a RVE.

III. RESULTS AND DISCUSSION

With the addition of nanotubes, viscosity of the polymer and nanotube mixture will dramatically increase and result in rapid drop of the shear dispersion efficiency. Thus uniform dispersion of nanotubes is limited to very low concentrations (usually less than 1 vol %) depending on the diameter and aspect ratio of the nanotubes. At low concentrations, individual CNTs are wet and surrounded by polymer molecules and the electrons can only conduct by quantum tunneling. The tunneling resistance among nanotubes depend on the polymer properties, the separation distance and the electronic properties of the nanotubes. Compared to the resistance of direct CNT contacts, the tunneling resistance will be orders larger in magnitude. Foygel et al. have estimated the average effective junction resistance due to tunneling among CNTs, which is about $10^{13}$ Ω in a typical insulating polymer matrix, by fitting their formula to the experimental results reported by Ounaies et al.

The tunneling resistance of a CNT-polymer-CNT junction can be estimated based on Simmons’s formula. Simmons’s equations predict the electrical tunneling resistance between two planar electrodes separated by a thin insulating layer. In this study, the junction is modeled as two planar electrodes separated by a polymer film with effective area of $d^2$.

The tunneling resistance between a CNT-polymer-CNT junction as a function of the thickness of the polymer layer can be expressed as:

$$s_1 = \frac{6}{K \varphi_0},$$

$$s_2 = s_1 \left[ 1 - \frac{46}{3 \varphi_0 K s + 20 - 2 V s K} \right] + \frac{6}{K \varphi_0},$$

where $\varphi_0$ is the height of the rectangular potential barrier (in volt), $s$ is the insulator layer thickness (in angstrom), $s_1$ and $s_2$ stand for the difference between the limits of the barrier at Fermi level, and $K$ is the dielectric constant of the insulating film material. According to Li et al., $\varphi_0$ can be approximated as the work function of CNTs in volts, and $V$ is the applied voltage across the thin film, which is given by

$$V = \frac{e s}{A \varepsilon_0},$$

where $e$ is electron charge and $\varepsilon_0$ is the permittivity of vacuum. The tunneling resistance is calculated as

$$R_t = \frac{v}{(J A)},$$

The work function of CNTs is assumed to be 5.0 eV and polymer matrix dielectric constant $K$ is assumed to be 3.98. The tunneling resistance of a SWCNT-polymer-SWCNT junction as a function of the thickness of the polymer layer for different nanotube diameters is reproduced in Fig. 4.

The calculation shows that the tunneling resistance, between two crossed CNTs separated by a 1 nm thick epoxy layer, ranges from around $3 \times 10^{10}$ to $5 \times 10^{11}$ Ω as the diameter of CNTs changes from 8 to 2 nm correspondingly. The resistance increases to $10^{19}$ Ω for a separation of 1.8 nm and the tube diameter of 2 nm. The size effect of polymer molecules was seldom considered during the calculation of the tunneling resistance in previous simulation studies. The diameter of typical polymer molecule is a few tenths of nanometer. For example, oligomers of polyethylene have a diameter of around 0.4 nm. The epoxy resins are polymerized from oligomers with epoxide end groups which are more complex than oligomers of polyethylene, so the diameter of the epoxy resin chain should be considered more than 0.4 nm. In the case of uniform dispersion, CNTs are separated and wrapped around by polymer chains. The minimum separation between CNTs will be the thickness of...
a double layer of polymer molecules, which is on the order of 1 nm. Therefore the tunneling resistances corresponding to an insulating film of 1 nm (i.e., from $3 \times 10^{10}$ to $5 \times 10^{11}$ $\Omega$) should be taken as the lower limit estimation of those across a CNT-epoxy-CNT junction when the tube has a diameter of 2 nm.

Now consider the intrinsic resistance ($R_{\text{tube}}$) of a CNT which is given by

$$R_{\text{tube}} = \rho \times \frac{L}{\pi R^2},$$

where $\rho$ is the nanotube resistivity, $L$ and $R$ are the length and the radius of the tube, respectively. The resistivity of conductive CNTs was reported to be as low as $5.1 \times 10^{-8}$ $\Omega$ $\text{m}$. The resistivity of a typical metallic CNTs is usually taken as $10^{-6}$ $\Omega$ $\text{m}$.5 Given this resistivity, the intrinsic tube resistance is around $10^6$ $\Omega$ for a nanotube with length of 3 $\mu$m and a diameter of 2 nm.9 It is apparent that the intrinsic tube resistance is much smaller as compared to the above tunneling resistance and therefore negligible.

The relatively small intrinsic SWNTC resistance in comparison with the tunneling resistance does not form a sufficient condition to neglect the tube resistance during the simulation. The unique configuration of the effective resistor network in nanocomposite is another determinant factor validating the simplification. Examination of the resistor network shows that any conduction path in the RVE consists of alternating tube resistors and tunneling resistors. In other words, two tunneling resistors have to be connected by a tube segment, and similarly, two tube resistors are always bridged by one tunneling resistor. This unique configuration of effective networks and fact that the tunneling resistors are much larger in value as compared to the tube intrinsic resistances justifies the simplification of only taking into account the tunneling resistance during the simulation.

Figure 5 demonstrates the contribution of the tube resistance to the calculation of the conductivity of nanocomposites with two assumed tunneling resistances ($R_{\text{tunnel}}$), $10^6$ and $10^{13}$ $\Omega$. The former value is the junction resistance measured between two CNTs in physical contact and the latter one is the estimated effective tunneling resistance of nanocomposites.8,10,11 Here both $R_{\text{tunnel}}$ and $R_{\text{tube}}$ are included in the calculation. A RVE of lateral size of 4 $\mu$m is used and all the tubes are assumed to have the same length (L) of 3 $\mu$m. The aspect ratio is set to be 100. If the junction resistances are assumed to be $10^6$ $\Omega$, the conductivity shows a strong dependence on the tube resistivity [Fig. 5(a)], especially when the value of $R_{\text{tube}}$ and $R_{\text{tunnel}}$ become comparable. However, if $R_{\text{tunnel}}=10^{13}$ $\Omega$, the variation in nanotube resistivity from $10^{-6}$ to $10^{-2}$ $\Omega$ m does not result in any appreciable RVE electrical conductivity change and the curves overlap with the $\rho=0$ curve [Fig. 5(b)]. Thus it is reasonable to ignore $R_{\text{tube}}$ in simulating the electrical conductivity of nanocomposites in the case of well dispersion.

By ignoring the resistance contribution from tubes, the computation efficiency can be significantly improved. As shown in Table I, the number of resistors in the effective networks can be reduced by more than half as a result of neglecting of tube resistances. In this sense, the computation is optimized.

With improved computation efficiency, it is possible to use 3D Monte Carlo simulation to calculate high aspect ratio nanofillers that resembles the actual CNTs used in experiments. Figure 6 shows the simulation results of the electrical conductivities for composites with nanofiller aspect ratios ranging from 600 to 1000. A RVE of lateral size of 4 $\mu$m is used and all the tubes are assumed to have the same length (L) of 3 $\mu$m. In the simulation, the value of tunneling resistances is set to be as small as possible, such that the tunneling resistance dominates the composite conductivity in the same network.

Table I. Comparison between the number of total resistors ($n_t$) in the effective network in a RVE and the number of tunneling resistors ($n_n$) that dominates the composite conductivity in the same network.

<table>
<thead>
<tr>
<th>Volume fraction of CNTs</th>
<th>$n_n$</th>
</tr>
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<tbody>
<tr>
<td>0.013 34</td>
<td>1644</td>
</tr>
<tr>
<td>0.016 68</td>
<td>2345</td>
</tr>
<tr>
<td>0.020 01</td>
<td>3361</td>
</tr>
<tr>
<td>0.023 35</td>
<td>4518</td>
</tr>
<tr>
<td>0.026 68</td>
<td>5957</td>
</tr>
<tr>
<td>0.030 02</td>
<td>7608</td>
</tr>
<tr>
<td>0.033 36</td>
<td>9318</td>
</tr>
<tr>
<td>0.036 69</td>
<td>11 323</td>
</tr>
<tr>
<td>0.040 03</td>
<td>13 571</td>
</tr>
</tbody>
</table>

Figure 5 demonstrates the contribution of the tunneling resistance during the simulation.

$\text{FIG. 5.}$ (Color online) Effect of the nanofiller resistivity on the total nano composites conductivity with different tunneling resistances when all resistors in the conductive path are included when: (a) $R_{\text{tunnel}}=10^6$ $\Omega$; (b) $R_{\text{tunnel}}=10^{13}$ $\Omega$.

$\text{FIG. 6.}$ (Color online) Critical behavior of the electrical conductivity ($\sigma$) as a function of CNT volume fraction ($\phi$) in cases of high aspect ratios. The data is replotted in the inset.
The results are consistent with the measurements of the electrical conductivity of SWCNTs reinforced polyimide composites reported by Oumaies et al. The contact resistance among tubes in one bundle, which can be approximated as the contact resistance multiplied by the tunneling resistance and the resistance of individual tubes, can have large variations as a function of the junction configuration and materials properties of nanotubes and polymer. Next step of the study is to consider these physical property variations in the simulations and try to make our models closer to real situations.

IV. CONCLUSIONS

In summary, for polymer nanocomposites consisting of uniformly dispersed conductive nanotubes and insulating matrix materials, the electrical conductivity is mostly determined by the tunneling resistance among neighboring nanotubes. The determinant role of tunneling resistance can be explained by two following factors: the large difference in the tunneling resistance and the resistance of individual nanotubes and the unique structure of resistor networks consisting of alternating these two types of resistors. This observation validates the simplification of the resistor networks by ignoring the nanotube resistance which leads to significantly improved computation efficiency in network resistance calculation. The critical behavior of the electrical conductivity above the percolation threshold of composites containing CNTs of high aspect ratios is studied, and the predicted conductance behavior is in good agreement with the classical percolation theory as well as the experimental measurement. In this simulation, the parameters characterizing the nanotube properties are assumed to be constant or follow simple distributions. In real material systems, physical parameters, such as the tunneling resistance, can have large variations as a function of the junction configuration and materials properties of nanotubes and polymer. Next step of the study is to consider these physical property variations in the simulations and try to make our models closer to real situations.

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