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A stochastic approach towards a predictive model on charge transport properties in carbon nanotube composites

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ABSTRACT

A probabilistic approach is taken towards modeling the electrical transport properties of carbon nanotube composite materials. A pseudo-random generation method is presented with the ability to generate 3-D samples with a variety of different configurations. Periodic boundary conditions are employed in the directions perpendicular to the transport to minimize edge effects. Simulations produce values for drift velocity, carrier mobility, and conductivity in samples that account for geometrical features resembling those found in the lab. All results show an excellent agreement to the well-known power law characteristic of percolation processes, which is used to compare across simulations. One of the main objectives of this study was to determine optimum simulation box-sizes that minimize size-effects without rendering the simulation unaffordable. The effect of sample morphology, like nanotube waviness and aspect ratio, on charge transport within CNT composites is also evaluated. The accurate prediction of conductive properties as a function of the physical characteristics of the composite material, will aid in the design of composites that can, for instance actively monitor structural changes due to compression, stretching, or even damage through their effect on the conductivity.

1. Introduction

In recent years, carbon nanotubes (CNTs) have been intensively studied as they are of interest for a number of technological applications due to their exceptional electrical, mechanical, and thermal properties [1–7]. The conjugated structure of CNTs allows electrons to disassociate from specific atoms and occupy delocalized electronic states. This, added to the fact that typical CNT lengths are of the order of electron mean free paths, leads to ballistic charge transport along the CNT's axial direction [1,4,6]. Conductivity values of single CNTs have been reported to be on the order of 10^5 S/m [8] to 10^6 S/m [9]. CNT exceptional electrical, mechanical, and thermal properties have been exploited in many studies to improve these properties in other materials. It has been observed that various polymers [10–22], ceramics [23,24], and epoxies [25–32] see enhancements in these properties when blended with CNTs to form composites [32–40]. The focus of this work is electronic transport in nanocomposites. In that regard, an accurate understanding of how CNTs modify electrical properties of an otherwise insulating matrix, can extend their utilization to applications such as electromagnetic interference shielding [41–48], electrostatic reduction [13], and strain sensing for structural health monitoring [27,49–61], to mention some examples.

Composites consisting of electrically conductive CNTs and an insulating matrix generally behave in close agreement with percolation theory [40,62–66]. At the critical CNT concentration (percolation threshold), conductive networks begin to form throughout the host matrix allowing charge transport through the previously non-conductive material and increasing the overall conductivity by several orders of magnitude. Materials previously not useful for electronic applications have exhibited conductivities ranging from 10^{-7}–10 S/m when mixed with CNTs, an increase of several orders of magnitudes, in some cases, when compared to the bare matrix [10,25,33,67–70].

A percolating material will typically follow the well-known power-law given by Eq. (1).

$$\sigma = \begin{cases} 0 & \varphi < \varphi_c \\ \sigma_c(\varphi - \varphi_c)^t & \varphi > \varphi_c \end{cases}. \quad (1)$$

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where φ is the filler concentration, φ_c is the critical concentration at which percolation occurs, σ_c is the conductivity of the nanoinsert, and t is the critical exponent. Given a particular system, its conductivity curve can be fit to Eq. (1) with σ_c, φ_c, and t to be used as fitting parameters [63,65]. The value of t found from various experimental studies ranges between 1 and 6, with the majority of the values being less than 4. However, no clear relationship between particular values for t and a sample's properties seems to exist. The review by Bauhoffer et al., by no means the only source, is found to be a good reference as it provides detailed information on the nature of the power law and the conductivity of CNT composites and interested readers may find it useful [11].

Various experimental studies have shown that functionalization [40,71–74], chirality [71,75], aspect ratio [17,62,71], host matrix material [11,76], CNT dispersion in the matrix [17,35,37–39,71,74,77], relative alignment [17,65,75] and other processing variables can all have a significant impact on the electrical properties of the composite. Since so many variables can play a role, accurate and predictive modeling is needed to better understand how each variable contributes to the nanocomposite properties and to assist in the design of these materials for specific applications.

There have been various models presented in the literature attempting to explain the mechanisms behind charge transport within CNT composites, a majority of which reduce the composite with randomly dispersed nanotubes (NTs) to a resistor network [17,30,78–83]. These models typically include a resistor for each CNT within the sample, resistors for CNT junctions, and resistors for the gaps separating CNTs, which can include quantum approximations. The goal is then to find an equivalent resistance for the entire sample. This approach is somewhat convenient as, for instance, the extremely difficult problem of finding the voltage drop in each junction is avoided. These models have been beneficial in helping understand how NT waviness, aspect ratio, tunneling barrier height, and agglomeration affect conductivity in composite samples, even though the implementation is limited to samples with relatively few NTs [17,78–83]. On the other hand, these models are unable to account for changes in conductivity when composites change shape due, for instance, to tension or compression, as the resistor's value needs to be adjusted each time. In addition, resistor network models can only account for complete paths, rendering them unable to describe some important phenomena such as charge traps, which are locations where charges become trapped within the sample and do not reach the electrodes. Certainly those paths do not contribute to the conductivity of the sample, but because their presence negatively affects conductivity, studying their effect is important to help in the design of nanocomposites. Charge-hopping models that study charge transport by allowing carriers to hop between sites within the material provide an alternative description and have been implemented to study various conductive polymer materials, but to the best of our knowledge, never for nanocomposites [84–87]. Furthermore, the approach selected in this work is justified by the experimental finding that conductivity in multiwall CNT composites is dominated by 3D hopping transport, where charges hop between conductive CNTs [88].

Therefore, in this article a model is introduced with the capability to study in depth how various material properties affect charge transport within CNT composites, both before and after percolation is reached. In-house routines have been developed to first generate virtual composite samples and then to study charge transport within those samples using a hopping algorithm. The model has the ability to study samples large enough, in terms of size and number of nanoinserts, to appropriately model system sizes in modern day micromanufacturing labs without periodic boundary conditions in the transport direction. This capability is used here to conduct a systematic study to determine the minimum dimensions necessary to provide enough topological diversity in the sample to eliminate (within statistical precision) size effects. It is determined that the simulation box should be at least 4–5 times larger than the NT length for conductive properties to be independent of the sample size within the statistical error. It has also been found that statistical variation decreases for samples with larger NT aspect ratio. Incorporated into this model are exceptional visualization capabilities through a program that has been developed in house, with details provided elsewhere [89].

2. Methodology

2.1. Sample generation

In order to study electrical properties of CNT composites, virtual samples are generated to a specific size and with specific NT volume concentrations using a Monte Carlo algorithm. To start the generation process, the simulation box is partitioned into a three-dimensional grid with the distance between each grid point equal to the specified NT diameter. A seed grid point is chosen randomly as the starting point for growing a NT, and a random walker then grows each NT segment by segment, in the x, y, or z direction, along the three-dimensional grid. The random walker starts at the seed grid point and then "walks" to neighboring points based off of probabilities defined by user-specified input parameters. Grid points define the start and end point of each of the segments that make up a NT, however, each segment can span a user-defined number of grid points. If a point that already hosts a segment is chosen for growth, the choice is rejected and the segment is regrown. Waviness is introduced by giving each new segment a probability to continue growing along the specified orientation or to deviate from that orientation. A waviness factor (WF) for the sample is defined as:

$$WF = 1 - \left(\sum_{i=1}^{N} \frac{\Delta D_i}{L_i} \right) \Big/ N \tag{2}$$

Here ΔD_i. is the distance along a straight line connecting the two ends of NT i, L_i is the length of NT i when stretched, and N is the number of NTs. Defined as in Eq. (2), a larger waviness factor indicates a sample with wavier NTs.

The algorithm to generate a nanocomposite sample that was described above is an adaptation of the method reported by Evans et al. [90]. In that work, aggregates of nanofillers were generated into a volume space using a Metropolis Monte Carlo method. Each nanofiller was considered one grid cell within the volume space

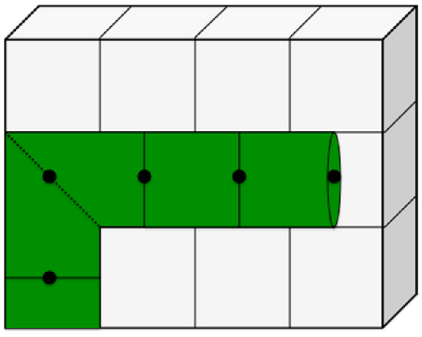

Fig. 1. Schematic representation of the segment-by-segment NT's growth process. New segments for a given NT are grown in consecutive grid cells.