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Three-Dimensional Monte Carlo Simulation of the Electrical Conductivity of Carbon Nanotube/Polymer Composites

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Monte Carlo simulations are performed to investigate the effects of the attractive intermolecular interaction, flexibility and size dispersity of carbon nanotubes (CNTs) on the electrical conductivity of CNT/polymer composites. We show that a flexibility plays an important role in the CNT agglomeration; rigid CNTs agglomerate readily for sufficiently strong attractive intermolecular interaction, while flexible CNTs do not. This is because more flexible CNTs are less likely to connect to neighbor CNTs. For weak attractive intermolecular interactions, however, the electrical percolation threshold concentration increases with increases in the flexibility and size dispersity, thus decreasing the electrical conductivity.

Composites of carbon nanotubes (CNTs) and polymers have been considered as a promising class of materials due to their high electrical conductivity and excellent mechanical strength.[1–4] However, the van der Waals interaction between CNTs is so attractive compared with the thermal energy such that CNTs agglomerate easily and disperse poorly in polymer matrices. This prevents CNTs from forming the electrical percolating network and deteriorates the electrical conductivity significantly, which has been a stumbling block to the application of CNT–polymer composites in industry. In order to reduce the strong van der Waals interaction between CNTs, the size of CNTs is adjusted via sonication or the surface of CNTs is modified.[5–10] However, such structural changes of CNTs result in an increase in either flexibility or size dispersity, which in turn may reduce the electrical conductivity.[8] It is an issue of importance, therefore, to find an optimal condition to maximize the electrical conductivity based on the understanding of the effects of the structure and intermolecular interaction on the electrical percolation behavior. In this work, we employ Monte Carlo simulations to investigate the electrical percolation behavior of CNTs while changing size dispersity, flexibility and intermolecular interaction of CNTs.

The electrical conductivity (σ) follows a well-known scaling relation, i.e., $\sigma \sim (\phi - \phi_c)^\gamma$, where ϕ and ϕ_c denote the volume fraction of CNTs and the value of ϕ at the percolation threshold, respectively, and γ is the scaling exponent.[1,11] ϕ_c is the minimum concentration of CNTs required to form a percolating network. If one can decrease ϕ_c, one may enhance the electrical conductivity and maintain the desired properties of polymer matrices such as the transparency and processability. In order to understand the effect of CNT structures on ϕ_c, therefore, there were many simulation and theoretical studies.[12–22] However, they were mostly limited to rigid rods without the flexibility and size dispersity properly implemented. Some simulation studies were carried out with predefined geometries. Recently, Lu *et al.* and Ma and Gao have proposed models of curved CNTs and found that ϕ_c increased significantly with an increase in the flexibility.[12,16] However, attractive intermolecular interactions (usually much stronger than the thermal energy) were ignored in their models, and the effect of the flexibility on the agglomeration could not be investigated.

The attractive intermolecular interactions between CNTs have been tuned by either modifying CNT surfaces or introducing depletants.[5] A recent theoretical study by Kyrylyuk and van der Schoot showed that as the intermolecular interactions of CNTs became more attractive, the percolating network structure would change significantly and ϕ_c should decrease.[17] Moreover, the entropically driven intermolecular attraction could increase the electrical conductivity of silver nanoparticles in polymer matrices by orders of magnitude.[23,24] Therefore, it should be an issue of importance in developing a simulation model that considers the intermolecular interactions between CNTs as well as their structure in order to fully elucidate the electrical percolation behavior of CNT/polymer composites.

We employ a coarse-grained model of CNTs with both the flexibility and van der Waals interactions considered. A CNT is modeled as a tangent hard sphere chain with a square-well (V_{sq}) interaction between beads of a well-depth $-\epsilon$ for $\sigma < r < \Delta$, where r is the distance between two beads, σ is the unit length, and $\Delta = 0.5$ in our simulations. The intermolecular interaction becomes more attractive with an increase in ϵ that in our study ranges from 0 to 0.2. A bending potential is also imposed among any pair of three consecutive beads connected via two chemical bonds, i.e., $V_a = \alpha[1 + \cos(\theta)]$, where θ is the angle between the two chemical bonds and α in our simulations ranges from 0 to ∞. CNTs are rigid rods when $\alpha = \infty$.

Initial configurations of CNTs are obtained by inserting CNTs sequentially (Fig. 1). A CNT is inserted at a random position and checked if the CNT overlaps with preexisting CNTs. If no overlap occurs, the random position is accepted and discarded otherwise. This procedure is repeated until a desired volume fraction $[\phi \equiv (MN\pi\sigma^3)/(6L^3)]$ is acquired, where M and N are the number of CNTs and the number of beads per CNT, respectively, and L is the dimension of the simulation cells. In our simulations, N and ϕ range from 16 to 64 and 0.001 to 0.1, respectively. M changes according to the values of N, ϕ, and L (= 40–150). We also generate configurations for binary mixtures of CNTs of two different N's with a mole fraction (x_l) of longer CNTs. The equilibrium configurations of CNTs are obtained via Monte Carlo simulations with a standard Metropolis algorithm. The system is evolved by moving a randomly chosen CNT at a time using a

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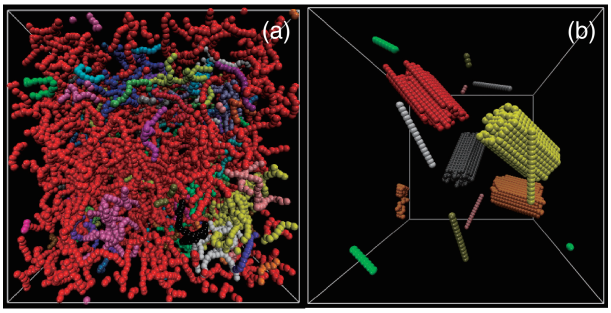

Fig. 1. Representative simulation snapshots for $N = 16$. (a) Red CNTs form a percolating network while CNTs of other colors are isolated from the percolating network ($\alpha = 5$ and $\phi = 0.026$). (b) Stiff CNTs ($\alpha = \infty$) form aggregates for $\epsilon = 0.225$ and $\phi = 0.021$.

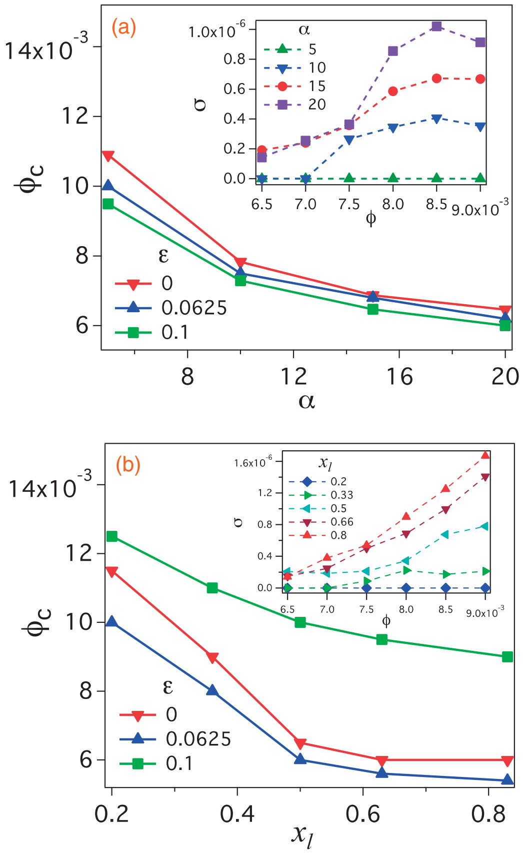

Fig. 2. Simulation results for ϕ_c for (a) flexible CNTs ($N = 64$ and $x_l = 1$) and (b) a binary mixture of rigid CNTs ($N = 16$ and 64). In the insets are the electrical conductivity σ for $\epsilon = 0.0625$ as a function of ϕ.

random move such as translation, rotation, reptation, and continuum configuration bias moves. For a given condition, up to hundreds of equilibrium configurations are obtained.

Two CNTs are considered connected when the shortest distance between them is smaller than the critical distance d_t, for which an electron may be transferred between those two CNTs via quantum mechanical tunneling. The value of d_t has not been estimated accurately either theoretically or experimentally. However, it has been found that d_t did not change the qualitative behavior of the electrical percolation network.[25)] In this work, $d_t = 0.5$. The cluster of connected CNTs is sought via a recursive algorithm and is examined whether the cluster is a percolating network or not. The periodic boundary condition is taken into account when examining for a percolating network. Then, the fraction (P) of equilibrium configurations with percolating networks is estimated. For a thermodynamic limit with $L = \infty$, P undergoes a discontinuous transition at the percolation threshold concentration ($\phi = \phi_c$). For finite L's as in our simulations, ϕ_c corresponds to the value of ϕ for $P = 0.5$. The electrical conductivity (σ) is estimated using Kirchhoff's current law and a resistor network model.[26)]

As CNTs become either more flexible or shorter due to the sonication and surface modification, the effective aspect ratio decreases significantly. It was reported that the effective aspect ratio could be controlled and decreased by up to about 70%.[6,9,27)] Such a decrease in the effective aspect ratio might increase ϕ_c, thus deteriorating the electrical conductivity. The effective aspect ratio of CNTs in our simulations decreases with a decrease in α or x_l. As depicted in Fig. 2, therefore, ϕ_c increases and σ decreases with a decrease in α or x_l for a given ϵ and ϕ.

As the intermolecular interaction becomes weakly attractive (or ϵ increases from 0 to 0.0625), ϕ_c decreases and σ increases slightly (Fig. 2), which is consistent with a previous theoretical work and simulation studies.[17)] A weak attractive interaction facilitates the formation of robust percolating networks, and for such a weak attractive interaction, the CNT agglomeration does not occur.

However, with a sufficiently strong attractive interaction, CNTs start agglomerating. Once CNTs agglomerate in simulations, they are frozen due to a strong attractive interaction. Then, it is not feasible in our simulation times to sample the whole phase space of the system. Thus, we repeat the simulations with many different initial configurations to confirm the agglomeration. With sufficiently large agglomerates formed, percolating networks vanish. For example, for rigid rods of $N = 64$ and $\phi = 0.01$, percolating networks form with $\epsilon < 0.2$, but the percolating network breaks down with agglomerates for a larger ϵ. And for a given size dispersity (or x_l), ϕ_c of rigid CNTs changes in a *non-monotonic* fashion with ϵ (Fig. 2). More interesting is that flexible CNTs do not agglomerate while rigid CNTs do for a given ϵ. For $\epsilon = 0.1$, ϕ_c of rigid CNTs with $\alpha = \infty$ becomes significantly larger than that of flexible CNTs with $\alpha < 20$. This result suggests that the flexibility could prevent the agglomeration.

As CNTs become more flexible, those CNTs are less likely to make contact with neighbor CNTs as depicted in Fig. 3. The site–site intermolecular correlation functions [$g(r)$] are larger for rigid CNTs than for flexible CNTs, which implies that the probability of a flexible CNT to connect with another CNT should be significantly decreased. Therefore, as long as CNTs do not agglomerate with a relatively weak attraction, flexible CNTs form a percolating network at a higher CNT concentration with a lower σ. However, when CNTs agglomerate with a strong attractive interaction, flexible CNTs are less likely to agglomerate than rigid CNTs because flexible CNTs do not make contact readily. This suggests that when the surfaces of CNTs are functionalized, the increased flexibility as well as the appended functional groups should hinder the agglomeration, which may help sustain the electrical percolating network.

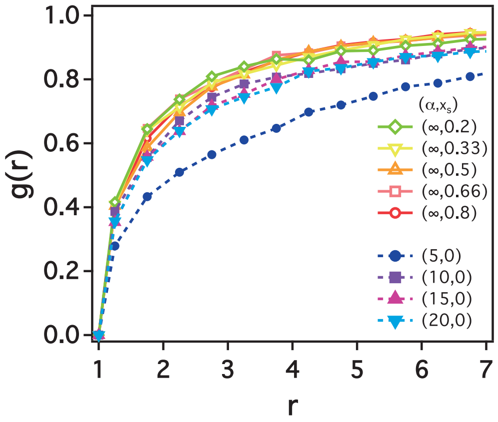

Fig. 3. Simulation results for the site–site intermolecular correlation functions $g(r)$ of binary mixtures of CNTs ($N = 64$ and 16) for $\epsilon = 0.0625$ and $\phi = 0.01$ for various values of x_l and α.

In summary, we present extensive Monte Carlo simulations using a coarse-grained model of CNTs with the flexibility, size dispersity and attractive intermolecular interactions taken into account. We find that the structure of CNTs affects the electrical percolation behavior significantly. As size dispersity or flexibility increases, the electrical percolation threshold concentration increases significantly resulting in a lower electrical conductivity. The effect of the CNT flexibility becomes subtle as the intermolecular interactions become more attractive. While rigid CNTs agglomerate easily with a sufficiently strong attractive interaction, flexible CNTs are less likely to connect to each other and form an aggregate, thus sustaining the electrical conductivity relatively well. Our simulation results illustrate that the flexibility should be taken into account when modeling the CNT/polymer composites. The general model in our simulations may be extended easily to investigate the electrical percolation behavior of polymer composites with other types of conductive fillers.

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