Investigation of Molecular Interactions between SWNT and Polyethylene/Polypropylene/Polystyrene/Polyaniline Molecules

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Single-walled nanotubes (SWNTs), which have a unique electronic structure, nanoscale diameter, high curvature, and extra-large surface area, are considered promising reinforcement materials for the next generation of high-performance structural and multifunctional composites. In the present study, force-field-based molecular dynamics simulations are performed to study the interaction between polymers and SWNTs. The “wrapping” of nanotubes by polymer chains was computed. The influence of temperature, nanotube radius, and chirality on polymer adhesion was investigated. Furthermore, the “filling” of nanotubes by polymer chains was examined. The results show that the interaction between the SWNT and the polymer is strongly influenced by the specific monomeric structure such as aromatic rings, which affect polymers’ affinities for SWNTs significantly. The attractive interaction between the simulated polymers and the SWNTs monotonically increases when the SWNT radius is increased. The temperature influence is negligible for polyethylene (PE) and polypropylene (PP) but strong for polystyrene (PS) and polyaniline (PANI). Also, our simulations indicate that the adhesion energy between the SWNT and the polymer strongly depends on the chirality. For SWNTs with similar molecular weights, diameters, and lengths, the armchair nanotube may be the best nanotube type for reinforcement. The simulations of filling reveal that molecules of PE, PP, and PS can fill into a (10, 10) SWNT cavity due to the attractive van der Waals interactions. The possible extension of polymers into SWNT cavities can be used to structurally bridge the SWNTs and polymers to significantly improve the load transfer between them when SWNTs are used to produce nanocomposites.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991,1 CNTs have attracted great research interest due to their unique properties such as high electrical and thermal conductivity, excellent stiffness against bending, and high tensile strength.2 Using CNTs as nanofibers to enhance the mechanical,3–10 electrical,11–14 thermal,15–17 and optical18 properties of composite materials has been pursued extensively both in experimental and theoretical studies.

Recently, experiments have shown remarkable enhancements in elastic modulus and strength of polymer composites with an addition of small amounts of CNTs.19–22 It is well established, from the research on microfiber-reinforced composites over the past few decades, that the structure and properties of the fiber–matrix interface play a major role in determining mechanical performance and structural integrity of composite materials. However, due to difficulties in devising experiments to study the CNT–polymer interface, molecular dynamics (MD) simulations have become increasingly popular in the investigations of reinforcement mechanisms in CNT–polymer composite systems.23 Many groups have investigated the interfaces in CNT–reinforced polymer composites using MD simulations.

For example, Liao et al.24 have studied the interfacial characteristics of a CNT–reinforced polystyrene (PS) composite system through molecular mechanics (MM) simulations and elasticity calculations. They found that the fiber/matrix adhesion comes from electrostatic, van der Waals interaction, mismatch in the coefficients of thermal expansion, and radial deformation induced by atomic interactions. Frankland et al.25 have investigated the influence of chemical cross-links between a Single-walled nanotube (SWNT) and a polymer matrix on the matrix–nanotube shear strength using MD simulations. The results suggest that load transfer and modulus of nanotube–polymer composites can be effectively increased by deliberately adding chemical cross-linking and inadvertent chemical bonding between nanotubes and polymer matrices during processing may be in part responsible for the enhanced stress transfer observed in some systems of this type. Wong et al.26 have studied local fracture morphologies of CNT/PS rod and CNT/epoxy film composites. Transmission and scanning electron microscopy examinations showed that these polymers adhered well to CNT at the nanometer scale. Some of the important interfacial characteristics that critically control the performance of a composite material were quantified through MM simulations and elasticity calculations. Multiwalled CNT morphology-related mechanical interlocking at the nanometer scale, thermal residual stresses, as well as a relatively cavity free surface for polymer adsorption are also believed to be contributing factors.

Gou et al.27 investigated the interfacial bonding of SWNT reinforced epoxy composites using a combination of computational and experimental methods. The interfacial shear strength between the nanotube and the cured epoxy resin was calculated to be up to 75 MPa, indicating that there could be an effective stress transfer from the epoxy resin to the nanotube. The following experimental results provided evidence of stress
transfer in agreement with the simulation results. Yang et al.\textsuperscript{28} have studied the interaction between polymers and CNTs using force-field-based MD simulation. They found that the specific monomer structure plays a very important role in determining the strength of interaction between nanotubes and polymers. The polymers with a backbone containing aromatic rings are promising candidates for the noncovalent binding of CNTs into composite structures, which can be used as building blocks in amphiphilic copolymers to promote increased interfacial binding between the CNT and the polymeric matrix. Wei\textsuperscript{29} has studied temperature-dependent adhesion behavior and reinforcement in CNT–polymer composite. They found that the interfacial shear stress through van der Waals interactions increases linearly with applied tensile strains along the nanotube axis direction and a lower bound value for the shear strength is found \(\sim 46\) MPa at low temperatures. Direct stress–strain measurements show significant reinforcements in the composite in a wide temperature range, with \(\sim 200\%\) increase in the Young’s modulus when adding a 6.5\% volume ratio of short CNTs.

However, most of the cited literatures considered the effect of only one or two factors on the adhesion properties. In this study, we focus on the physisorption of polymers on SWNTs and investigated the physical interactions between polymers and SWNTs in all conditions that we could think about using MD simulations.

2. Experimental Section

2.1. Computational Method. In this study, MD simulations were conducted to explore the interaction between SWNTs and polymers. The wetting properties of the SWNTs and the polymers were also studied based on the MD results, through which we could obtain useful information for the development of nanotube-based polymeric composites. Here, MD simulations were carried out with a commercial software package called Materials Studio developed by Accelrys Inc. The condensed phase optimization molecular potentials for atomistic simulation studies (COMPASS) module in the Materials Studio software was used to conduct force-field computations. The COMPASS was a parametrized, tested, and validated first ab initio force field,\textsuperscript{30,31} which enables an accurate prediction of various gas-phase and condensed-phase properties of most of the common organic and inorganic materials.\textsuperscript{32–34}

Here, the MD simulation for each case study was performed long enough to observe several cycles of thermal vibration. The interval of each MD simulation step was typically 1 fs. All calculations were carried out at the initial temperature of 400 K except special conditions, using a constant number of particles, constant volume, and constant temperature (NVT) ensembles.

2.2. Force Field. The application of quantum mechanical techniques can accurately simulate a system of interacting particles, but such techniques often cost too much time and are usually feasible only in systems containing up to a few hundred interacting particles. As we know, the main goal of simulations of the systems containing a large number of particles is generally to obtain the systems’ bulk properties which are primarily controlled by the location of atomic nuclei, so the knowledge of the electronic structure, provided by the quantum mechanical techniques, is not critical. Thus, we could have good insight into the behavior of a system if a reasonable, physically based approximation of the potential (force-field) can be obtained, which can be used to generate a set of system configurations which are statistically consistent with a fully quantum mechanical description. As stated above, a crucial point in the atomistic simulations of multiparticle systems is the choice of the force fields, a brief overview of which is given in this section.

In general, the total potential energy of a molecular system includes the following terms:\textsuperscript{35}

\[
E_{\text{total}} = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{non-bond}}
\]

\[E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{coop}} + E_{\text{UB}}\] (2)

\[
E_{\text{cross-term}} = E_{\text{bond-bond}} + E_{\text{angle-angle}} + E_{\text{bond-angle}} + E_{\text{end-bond-torsion}} + E_{\text{middle-bond-torsion}} + E_{\text{angle-torsion}} + E_{\text{angle-angle-torsion}}
\]

\[E_{\text{non-bond}} = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{H-bond}}\] (4)

The valence energy generally includes a bond stretching term, \(E_{\text{bond}}\), a two-bond angle term, \(E_{\text{angle}}\), a dihedral bond-torsion term, \(E_{\text{torsion}}\), an inversion (or an out-of-plane interaction) term, \(E_{\text{coop}}\), and a Urey–Bradley term (involves interactions between two atoms bonded to a common atom), \(E_{\text{UB}}\).

The cross-term interacting energy, \(E_{\text{cross-term}}\), accounts for the effects such as bond lengths and angles changes caused by the surrounding atoms and generally includes the following: stretch–stretch interactions between two adjacent bonds, \(E_{\text{bond-bond}}\); bond–angle–bond–angle interactions between two valence angles associated with a common vertex atom, \(E_{\text{angle-angle}}\); stretch–tensors interactions between a dihedral angle and one of its bonds, \(E_{\text{bond-angle}}\); stretch–torsion interactions between a dihedral angle and one of its end bonds, \(E_{\text{end-bond-torsion}}\); stretch–torsion interactions between a dihedral angle and its middle bond, \(E_{\text{middle-bond-torsion}}\); torsion interactions between a dihedral angle and one of its valence angles, \(E_{\text{angle-torsion}}\); and bond–bond–torsion interactions between a dihedral angle and its two valence angles, \(E_{\text{angle-angle-torsion}}\).

The nonbond interaction term \(E_{\text{non-bond}}\) accounts for the interactions between nonbonded atoms and includes the van der Waals energy, \(E_{\text{vdW}}\), the Coulomb electrostatic energy, \(E_{\text{Coulomb}}\), and the hydrogen bond energy, \(E_{\text{H-bond}}\).

The COMPASS force field uses different expressions for various components of the potential energy as follows:\textsuperscript{32,33}

\[
E_{\text{bond}} = \sum_b K_b(b - b_0)^2 + K_b(b - b_0)^3 + K_d(b - b_0)^4
\] (5)

\[
E_{\text{angle}} = \sum_\theta H_\theta(\theta - \theta_0)^2 + H_\theta(\theta - \theta_0)^3 + H_\theta(\theta - \theta_0)^4
\]

\[
E_{\text{torsion}} = \sum_\phi \{V_\phi[1 - \cos(\phi - \phi_1^\phi)] + V_\phi[1 - \cos(2\phi - \phi_2^\phi)] + V_\phi[1 - \cos(3\phi - \phi_3^\phi)]\}
\] (7)

\[
E_{\text{coop}} = \sum_b K_b \chi^2_b
\] (8)

\[
E_{\text{bond-bond}} = \sum_b \sum_{b'} F_{bb'}(b - b_0)(b' - b_0)
\] (9)

\[
E_{\text{angle-angle}} = \sum_\theta \sum_{\theta'} F_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta_0')
\] (10)
2.3. Molecular Model. 2.3.1. Molecular Model of SWNT. In this study, the molecular models of SWNTs with different diameters and chirality were established with use of Materials Studio. The electronic structures of the all carbon atoms in the SWNT models were $sp^2$ hybridization. The unsaturated boundary effect was avoided by adding hydrogen atoms at the ends of the SWNTs. Each C–C bond length was 1.42 Å and each C–H bond length was 1.14 Å. The hydrogen atoms had charges of +0.1268 e and the carbon atoms connecting hydrogen atoms had charges of −0.1268 e, thus the neutralized charged SWNTs were constructed. The computer graphics picture of a (10, 10) SWNT model (400 carbon atoms and 40 hydrogen atoms) is shown in Figure 1.

2.3.2. Molecular Model of the Investigated Polymers. The simulated polymers were polyethylene (PE), polypropylene (PP), PS, and polyaniline (PANI). The chemical structures are provided in Figure 2. To make a direct and comparable measurement of the interaction energies between SWNTs and polymers, the simulated models of the polymers were selected with comparable numbers of atoms and molecular weights (PE 38 atoms, 170; PP 38 atoms, 170; PS 34 atoms, 204; and PANI 26 atoms, 184). The number of atoms and monomers used is small (about 35 atoms per molecule, which corresponds to 6 monomers for PE, 4 monomers for PP, 2 monomers for PS, and half a monomer for PANI) and hence the results of our simulation describe the behavior of the small part of the whole polymer. However, the term “polymer” was used throughout the paper for simplicity. PE is polymeric molecules with no side groups, whereas PP has side groups of methyl. PS and PANI are both molecules with groups of aromatic radicals.

3. Results and Discussion

Generally speaking, wrapping and filling are two typical phenomena which would take place when the interactive process of the SWNT–polymer system is simulated. Constant NVT simulations were carried out with undefined boundary conditions in a relatively short simulation time (several nanoseconds). The polymer would move away eventually and very likely never interact with the CNT again if the simulation time were long enough, which is a direct consequence of the fact that we use infinite volume (no boundary conditions). However, this “escape” event is extremely rare and it does not affect the results within our simulation time.

3.1. Wrapping. Polymer wrapping of CNTs has received attention as a promising way for manipulating and organizing SWNTs into ordered structures and improving their dispersion into the matrix of the composites. Recently, Chen et al. have reported a controlled and nanotube-specific method for immobilizing proteins and small biomolecules onto noncovalently functionalized SWNTs. Experiments for the wrapping of SWNTs with poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) have also been reported. To simulate the interaction between polymers and SWNTs, MD simulations were established with the polymers initially placed at the side of the SWNTs within a distance of 9.5 Å, which is the cutoff distance of van der Waals interactions in this study.

3.1.1. Interaction between Polymers and SWNTs. First, an armchair (10, 10) SWNT (Figure 1) and four polymer models are selected as the representative elements for the simulation. Figures 3–6 show the snapshots of polymers and SWNTs observed at different time steps of the simulation. Initially, the polymer chains were put near the middle of SWNTs in a distance of about 8.5 Å. The simulation showed that all four molecular chains would stretch and move toward the nanotube until they finally wrapped on the surface of the helix of the nanotube and the equilibrium was achieved. Particularly, it cost about 70 ps for the wrapping of PE, PP, and PS, but only 5 ps for PANI, which may be because of the strong polarity of PANI. We also noticed that the aromatic rings of PS and PANI molecules gradually orientated to align their ring planes parallel to the SWNT surfaces during the dynamic interactions.

The dynamic behavior of the polymer molecules can be illustrated by tracking the interaction energy of the SWNT–polymer molecules. Generally, the interaction energy is estimated from the difference between the potential energy of the
The total potential energy of the composite can be expressed as follows:

\[
\Delta E = E_{\text{total}} - (E_{\text{SWNT}} + E_{\text{polymer}})
\]

where \(E_{\text{total}}\) is the total potential energy of the composite, \(E_{\text{SWNT}}\) is the energy of the nanotube without the polymer, and \(E_{\text{polymer}}\) is the energy of the polymer without the nanotube. In other words, the interaction energy can be calculated as the difference between the minimum energy and the energy at an infinite separation of the nanotube and the polymer matrix. \(^{23,27,40}\)

Figure 7 shows the potential energies during the simulation and we can find that the potential energies of the four composites are almost the same during the simulations. Figure 8 shows the interaction during the wrapping process for PE, PP, PS, and PANI. Initially, for all the polymers the interaction between SWNTs and polymer chains gradually increases. For PE and PP, the attractive interaction increases to \(-13\) kcal/mol, while for PS and PANI it increases to \(-20\) kcal/mol, which is much stronger. Both PS and PANI are molecules with groups of aromatic rings, for PS in the side and for PANI in the backbone, so the interaction energy between polymers and SWNTs may be greatly influenced by aromatic rings. \(^{3.1.2}\)

### 3.1.2. The Influence of Different Factors on Polymer Adhesion.

First, we put different polymer chains near the nanotube to save simulation time, then the MD simulations were carried out to study the interaction between SWNTs and individual molecules of PP, PE, PS, and PANI for 200 ps. After this, the systems were minimized to achieve the strongest bonding between the nanotubes and the polymers with use of MM simulations. Then, MD simulations were carried out for another 100 ps and the total interaction energies between the SWNTs
and the polymers were recorded every 5 ps. Finally, averages were calculated to get rid of the fluctuations during the simulations.

Influence of the Temperature on Polymer Adhesion. To assess the temperature dependence of the adhesion energy between the polymers and the SWNTs, some MD simulations were carried out at different temperatures, which varied from 300 to 500 K in steps of 25 K. Figure 9 shows the temperature dependence of the intermolecular interaction. It was shown that the interaction decreases weakly with increasing temperature for PE and PP, so the temperature influence is neglectable. However, for PS and PANI, the interaction decreases strongly with increasing temperature, which may be caused by the aromatic rings in polymers.

Influence of the Nanotube Radius on Polymer Adhesion. To determine the influence of the nanotube radius on polymer adhesion, some MD simulations were carried out on SWNTs with PE, PP, PS, and PANI, respectively. The SWNT radius was varied from 8.14 to 27.12 Å in these simulations. The simulations show that the attractive interaction between the simulated polymers and the SWNTs monotonically increases when the SWNT radius is increased. Especially, for PS and PANI, the interaction is much stronger and increases more rapidly than that of PE and PP. PS and PANI are both polymers with aromatic rings, which are therefore expected to possess a strong attractive interaction with the surface of the SWNTs and may play an important role in providing effective adhesion. When the SWNT radius is increased, aromatic rings in polymers can well align parallel to the surface, and thus the interactions between the aromatic rings and the SWNTs increases significantly as shown in Figure 10.

Influence of the Nanotube Chirality on Polymer Adhesion. In this part of our study, the initial atomic configurations of SWNTs are obtained by creating the planar hexagonal carbon atom network corresponding to an \((n, m)\) nanotube cut open axially. The corresponding chiral angle \(\theta\) and diameter \(D_n\) of a
SWNT with \((n, m)\) indices could be determined by using the rolling grapheme model:

\[
\theta = \arctan\left(\frac{\sqrt{3}m}{2n + m}\right) ; D_n = \sqrt{\frac{3}{\pi}}b\sqrt{(n^2 + m^2 + nm)}
\]

\((0 \leq m \leq n) \) (19)

where \(b\) is the C–C bond length.\(^{23}\) The unsaturated boundary effect is also avoided by adding hydrogen atoms at the ends of the SWNTs. Eight types of SWNTs, with different chirality but similar molecular weights, diameters, and lengths, are generated as shown in Figures 1 and 11. The total number of atoms, diameters, and lengths for each chiral nanotube are presented in Table 1.

Figure 12 shows the adhesion energy of the composite versus the corresponding chirality of the nanotube. It was shown that the adhesion energy decreases when the chiral angle becomes smaller for the SWNTs with different chirality. Therefore, the adhesion energy between the SWNTs and the polymers strongly depends on the chirality and the armchair SWNT is the best nanotube type for reinforcement. Chirality dependent conformation of the polymer molecule at the nanotube interface has been investigated through MD simulations by Wei.\(^{41}\) The local wrapping angle \(\theta\) is defined as the angle between the vector connecting the two ends of a three-segment subchain on a polymer molecule and the nanotube axis. The simulations indicated that, while wrapping around \(0^\circ\) dominates on a small radius armchair SWNT, molecule wrapping shifts to larger angles on a similar radius zigzag tube. The different conformations of polymer molecules at various SWNT interfaces may cause different interaction energy and the armchair SWNTs may have the strongest interaction with the polymers.

3.2. Filling. The possibility of filling polymers into nanotubes during real-world composite processing would create the desired structure bridges between nanotubes and polymers. However, the reality of this filling will be mainly determined by van der Waals interactions between the polymers and the internal surfaces of the SWNTs. To study the four polymer molecules’ filling phenomena, some MD simulations were set up with the polymer chains initially placed near the opening at one end of the nanotubes along the direction of the nanotube axis.

The simulations show that molecular chains of PE, PP, and PS would gradually move all the molecular bodies into the nanotubes, while PANI molecule cannot encapsulate into the nanotube even after a long simulation time, which may be caused by the strong polarity of PANI. The configurations of PE, PP, and PS molecules filling into SWNTs, which is observed at different time steps of the MD simulations, are shown in Figures 13—15. For PE and PP, the molecules were lingering around the opening first, then constantly changing their orientation to facilitate filling into the SWNT opening, and encapsulating into the nanotubes within 100 ps. An equilibrium state of the system was also achieved when the polymer molecules were entirely in the nanotubes. However, as shown in Figures 13 and 14, we also notice that the PE molecule will stay in the middle of the nanotube, while the PP molecule will stay near the opening instead of going to the middle of the nanotube or the opposite opening, which may be because PP has side groups of methyl and is not as smooth as the PE molecular chain. For PS, however, a very slow filling process is observed compared with the fast filling phenomenon of PE and PP, which cost about 2000 ps as shown in Figure 15. The PS chain has side groups of aromatic rings, which may be an important factor for the slow filling.

Figure 16 shows the potential energies and interaction energies during the simulations and we can see that the potential energies of the four composites are also almost the same during the simulations. Figure 17 shows the interactions during the filling process for PE, PP, PS, and PANI. Initially, just as in the wrapping process, for all the polymers the interaction between SWNTs and polymer chains gradually increased until they encapsulated into the nanotube and achieved an equilibrium state. We also notice that the interaction energy will increase rapidly for PE, PP, and PS once they start filling the nanotube, which reveals that the filling can improve the load transfer between polymers and SWNTs significantly.
4. Conclusions

In this study, some MD simulations are carried out to investigate the interaction of PE, PP, PS, and PANI molecules with SWNTs in a vacuum. The results show that the interaction between the SWNT and the polymer is strongly influenced by the specific monomer structure such as aromatic rings, which affects the polymers’ affinities for SWNTs significantly. The results also show that the attractive interaction between the simulated polymers and the SWNTs monotonically increases when the SWNT radius is increased. The temperature influence is neglectable for PE and PP but strong for PS and PANI. The MD simulations also indicate that the adhesion energy between the SWNT and the polymer strongly depends on the chirality and the armchair nanotube is the best nanotube type for reinforcement. Last, the filling simulations reveal that molecules of PE, PP, and PS can fill into a (10, 10) SWNT cavity due to the attractive van der Waals interactions. The possible extension of polymers into SWNT cavities can be used to structurally...
bridge the SWNTs and polymers to significantly improve the load transfer between them when SWNTs are used to produce nanocomposites.

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References and Notes