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Interaction between single-walled carbon nanotubes and polymers: A molecular dynamics simulation study with reactive force field

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ABSTRACT

Mixtures of Single-Walled Carbon Nanotubes (SWNTs) and polymers play an important role in practical applications such as ultrastrong lightweight materials and organic solar cells. In present work, we studied the interaction between SWNTs and polymers including poly(3-hexythiophene) (P3HT), Poly(2-methoxy-5-(3-7-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV), and Poly[[[(2ethylhexyl)oxy]methoxy-1,4-phenylene]-1,2-ethenediyl] (MEH-PPV) by molecular dynamics (MD) simulation. For the first time, we use molecular dynamics simulation based on a reactive force field (ReaxFF) to study the interaction between polymers and SWNTs. Interaction energy between polymers and SWNTs was calculated. Morphology of polymers adsorbed to the surface of SWNTs was investigated by the radius of gyration (R_g). Influence of temperature, SWNT radius, and chirality on interfacial adhesion of SWNT-polymer and R_g of the polymers were studied. Our results showed that the strongest interaction between the SWNTs and these polymers was observed first for P3HT, then MDMO-PPV, and finally MEH-PPV. We found that the interaction energy is influenced by the specific monomer structure of the polymers, SWNT radius, and chirality, but the influence of temperature is very weak. The temperature, radius, and chirality have not any important effect on the radius of gyration.

1. Introduction

Carbon Nanotubes (CNTs) have unique properties such as high electrical and thermal conductivity, thus they play a very important role in new technologies and science. CNTs can change optical [1], thermal [2–4], electrical [5–8], and mechanical [9–14] properties of composite materials. They can increase the strength of polymer composites and elastic modulus [15–18]. CNT–polymer composites have great potential as ultrastrong lightweight materials [19]. We know that the properties and structure of the SWNT–polymer interface play a main role in determining mechanical and electrical performance. To increase the Young's modulus and strength of CNTs–polymer composites, we must have a good interfacial binding for an efficient load transfer from the polymer matrix to CNTs.

It is hard to study the SWNT–polymer interface by experimental methods, thus many people use the molecular simulation methods. There are two methods of molecular simulation to study the interface between CNT–polymer: ab initio quantum mechanics [20,21], and molecular dynamics (MD) with force fields. Ab initio methods give more accurate results than MD, but these methods are computationally expensive for large molecular systems. MD methods are much faster than ab initio methods, thus many groups use MD to study the SWNT–polymer interface. For example, Liao and Li [22] reported the interfacial properties of SWNT and polystyrene (PS) composite using MD. Their results showed that the SWNT–polymer adhesion comes from the noncovalent intermolecular interactions between polymers and CNTs such as Van der Waals and electrostatic. They calculated the interfacial shear stress of the CNT/PS about 160 MPa.

Frankland et al. [23] have studied the effect of chemical cross-links between a polymer matrix and a SWNT on the matrix–nanotube shear strength using MD. Wong et al. [24] have investigated local fracture morphologies of CNT/PS rod and CNT/epoxy film composites. Gou et al. [25] reported the interfacial bonding of SWNT reinforced epoxy composites using computational methods. They calculated the interfacial shear strength up to 75 MPa. Yang et al. [26] have investigated the interaction between a SWNT and PS/poly (p-phenylenevinylene) (PPV)/poly (phenylacetylene) (PPA) using MD simulation. Their results showed that the monomer structure plays a very sensitive role in determining the strength of interaction between SWNT and polymers. They reported that the polymers with aromatic rings are good choice for the noncovalent binding of CNTs into composite structures. In another work, Zheng et al. [27] simulated the interaction energy between polyethylene (PE)/polypropylene (PP)/PS/polyaniline (PANI) and a SWNT. Their results were similar to the

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Yang group. Xie et al. [28] reported the influence of temperature, radius, and chirality on the interaction between SWNTs and fluorocarbon resins. Their results showed that the interactions between the SWNTs and fluorocarbon resins are not influenced by chirality and temperature but strongly depend on the radius of SWNTs.

These studies cannot show macroscopic nanocomposite properties, but they can show an obvious view of the interface between polymers and SWNT. All pervious works used a nonreactive force field such as PCFF, COMPASS [29,30], and MM3 [31]. These force fields cannot describe the destruction and construction of chemical bonds in the simulation systems and thus you must build the correct chemical bonds in the system. A reactive force field, ReaxFF, is a bond-order dependent force field that includes covalent interactions via bond-orders. REAX force field was used to many organic materials and its results are close to ab inito results [32–35]. In this work, we used MD simulation with REAX Force field to study the interaction between SWNTs and three conjugated polymers including P3HT, MDMO-PPV, and MEH-PPV. So far there has not been any simulation results reported for these polymers with SWNTs. Conjugated polymers show good binding with SWNT, and electron microscopy studies have demonstrated heavy coating of SWNTs by conjugated polymers [36]. In addition, blends of SWNTs and these polymers are used commonly as active materials in organic solar cells [37]. In this type of organic solar cells, these polymers are used as a donor material with SWNTs as an acceptor material. The interface structure and interaction energy play a major role in facilitating of charge transfer between donor and acceptor, and they affect on the efficiency and life time of solar cells [38]. Experimental results show that all P3HT backbone aligns parallel to the SWNT surface, and this increases the overall SWNT-polymer interaction [39].

2. Simulation method

Our MD simulations were done with free molecular dynamics software called LAMMPS. We used ReaxFF that is implanted in LAMMPS [40]. ReaxFF is a bond-order dependent force field that includes covalent interactions via bond-orders. The bond-order is calculated from the distances between atoms that are updated in molecular dynamics simulation in every step, thus allowing creation and breaking of chemical bonds. In addition to covalent interaction, this force field includes Coulomb and Van der Walls interactions commonly present in classical force field such as PCFF, COMPASS, and MM3. The total potential energy is calculated as the sum of various terms including:

$$E_{total} = E_{bond} + E_{over} + E_{val} + E_{tors} + E_{VdWaals} + E_{Coulomb} \quad (1)$$

Where E_{bond}, E_{over}, E_{val}, E_{tors}, $E_{VdWaals}$, and $E_{Coulomb}$ are the energies corresponding to bond, overcoordiniation, angle, torsion, Van der Walls, and coulomb interaction, respectively [32–35].

The molecular models of SWNTs with different dimensions were built with use of VMD software. The dimensions and chiral angles of the different SWNTs are showed in Table 1. We make all SWNTs with a fixed length of 73 Å and diameters ranging from 12.2 to 27.12 Å. We added hydrogen atoms at the ends of the SWNTs for avoiding the unsaturated boundary effect. To make a comparable measurement of the interaction energies, the polymers were selected with comparable numbers of atoms (P3HT 152 atoms; MEH-PPV 131 atoms; and MDMO-PPV 149 atoms, which correspond to 6 monomers for P3HT, 3 monomers for MEH-PPV and MDMO-PPV). Fig. 1 shows chemical structure of the investigated polymers. All polymers were placed at the side of the SWNTs within a distance of 9 Å.

All the simulations are done in the constant temperature and constant volume canonical ensemble (NVT). The equations of motions were integrated using Verlet algorithm with integration time step of 1 fs and the temperature is controlled by a Nosé–Hoover thermostat. The simulation system was equilibrated for 50 ps to stabilize the interaction. After this stage, the total intermolecular interaction energy was recorded for 50 ps with an interval of 1 ps. Finally, averages were computed to get rid of the fluctuation during the simulation.

Table 1
Dimensions of the SWNTs investigated in the simulations.

Type of SWNT	Diameter (Å)	Length (Å)	chiral angle θ (°)
(9,9) armchair	12.2	73	30
(10,10) armchair	13.56	73	30
(12,12) armchair	16.27	73	30
(14,14) armchair	18.98	73	30
(15,15) armchair	20.34	73	30
(17,17) armchair	23.05	73	30
(20,20) armchair	27.12	73	30
(119)	13.58	73	26.71
(12,8)	13.65	73	23.43
(13,7)	13.76	73	20.18
(14,5)	13.36	73	14.71
(15,4)	13.58	73	11.52
(16,2)	13.38	73	5.82
(17,0) zigzag	13.31	73	0

3. Results and discussion

3.1. Warpping

Figs. 2–4 represent snapshots of SWNTs and polymers at different time steps of the simulation. The simulation showed that all three polymers would stretch and move toward the SWNT until they wrapped on the surface. Particularly, it cost about 30 ps for the wrapping of MDMO-PPV and MEH-PPV, but only 14 ps For P3HT. These figures show that ReaxFF can build chemical bonds correctly between SWNT and polymer. The dynamic behavior of the polymers can be showed by drawing the interaction energy of the SWNT–polymer. The interaction energy is calculated from the difference between the potential energy of the composite and the potential energy for the polymer and SWNT as follows:

$$E_{interaction} = E_{total} - E_{\mathrm{SWNT}} - E_{polymer} \quad (2)$$

where E_{total} is the total potential energy of the system, E_{SWNT} is the potential energy of the SWNT without the polymer, and $E_{polymer}$ is the potential energy of the polymer without SWNT. In other words, we can compute the interaction energy as the difference between the minimum energy and the energy at an infinite separation of the polymer matix and the nanotubes. Fig. 5 shows the potential energies during the simulation and we can see that the simulation system was equilibrated. In addition, as the figure shows, P3HT has the strongest potential energy with the SWNT, then MDMO-PPV and MEH-PPV.

3.2. Influence of the temperature, radius and chirality on the interaction energy

To study the temperature dependence of the interaction energy, MD simulations were performed at different temperatures for SWNT (10,10) and the polymers. The temperature was increased from 300 to 500 K in steps of 25 K. Fig. 6 shows the temperature dependence of the interaction energy. The interaction decreases weakly with increasing temperature, thus the temperature influence is very weak in this range. It is due to the strong interaction between SWNT and polymer that cannot be influenced by the temperature. We can see that P3HT exhibits the strongest interaction