Molecular dynamics simulation for mechanical properties of CNT/Polyethylene composites

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Abstract. The pull-out process of the carbon nanotube from polyethylene was simulated by molecular dynamics method. A model of a carbon nanotube in polyethylene was established. In the simulation, Adaptive Intermolecular Reactive Empirical Bond Order (ARIEBO) potential was adopted to describe the interaction of C-C and C-H in the carbon nanotube and polymer, and Lennard-Jones pair potential was used to describe the interaction between the carbon nanotube and polymer; NVT ensemble was adopted in the whole simulation and Nose-Hoover method was used to control the temperature at absolute zero, which avoided the influence induced by thermal activation; Verlet algorithm was used to solve molecular dynamics equations in the procedure of simulation. The deformation and forces on interfaces between the carbon nanotube and polymer was analyzed by simulating the process of pulling-out of the carbon nanotube from polyethylene.

Keywords. carbon nanotube, molecular dynamics, potential function, polyethylene.

1. Introduction
Carbon nanotube has typical layered hollow structure and light weight as one-dimensional nanomaterial. Its hexagonal structure is perfectly connected and it has quite high slenderness ratio, usually greater than 1000. The unique structure makes it have excellent mechanical, electrical, thermal and chemical performances. Once discovered, carbon nanotube caused comprehensive interest and concern of researchers in academia and industry field because of its unique performance. Comprehensive concern is provoked on the increment of carbon nanotube synthetic ratio, the purification, opening, cutting, filling and the polymerization between carbon nanotube and polymer. Since 1994 Ajayan[1] mixed carbon nanotubes as inorganic filler into polymer matrix and to prepare polymer composite materials, a lot of work is done to make carbon nanotube evenly scattered in the polymer matrix by nano-composite technology which is in order to produce newly high-property and multi-functioned polymer matrix nano-composite materials. Composites in which carbon nanotube is the reinforcement reflect extensive application prospects on information materials, biomedical materials, high-performance structural materials, multi-functional materials and so on. Great progress has been made in the mechanical properties, thermal properties and function of CNT/polymer composites. Schadler[2] et al researched tension and compression property of MWNT/epoxy resin composites, a fact that compression modulus of composite materials was larger than tensile modulus was found, which was because only the outer of carbon nanotube transferred load when it was tensile, while both inner and outer woke when compression. Cooper[3] et al did pull-out experiment on a single carbon

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nanotube which crossed the hole of matrix by atomic force microscope and directly found interface strength between multi-wall carbon nanotube and epoxy resin is 35-376MPa. Biercuk\cite{4} et al found that thermal conductivity of CNT/epoxy resin composite material increased about 120% when 1% percent of carbon nanotubes were added. Wei\cite{5} et al found that heat exchange and diffusion coefficient of composites was improved after adding carbon nanotube by using molecular dynamics method. Mechanical properties of CNT/Si composites increased two times when volume fraction ratio of carbon nanotubes in composites was 0.01 found by Dalton\cite{6} et al. Lei\cite{7} et al tested the mechanical properties of CNT/epoxy resin composites at normal and elevated temperature. Sharon\cite{8} et al studied the mechanical properties of CNT/polystyrene and how irradiation affected the surface structures under argon irradiation. Zheng\cite{9} et al studied interface adhesion of different kinds of CNT/polymer using molecular mechanics and molecular dynamics. Because of special mechanical properties of carbon nanotube reinforced polymer composites, a model of a carbon nanotube in polyethylene was built and the process of pulling out of carbon nanotube from polyethylene was simulated by using molecular dynamics method in this article. Then polymer interfaces were analyzed from microcosmic angle and the force on carbon nanotube was calculated.

2. Model and method of simulation

2.1. Build the model

Carbon nanotube has periodicity in axial direction. The configuration of carbon nanotube can be shown by \((m, n)\) which decides the diameter, helix angle, lattice constant and physical properties exclusively. Polyethylene is made of a great many of ethylene chains. The whole model is built in Materials Studio in this article. Firstly, carbon nanotube of \((6, 6)\) is built. Its radius is 0. and the length is 1.476nm. Then, polyethylene chains are built. At last, carbon nanotube is placed in polyethylene, and the polyethylene chains in carbon nanotube are deleted (Figure 1.).

\[ m_i \frac{\partial^2 r_i}{\partial t^2} = F_i \]  

\( m_i \) is the quality of an atom, \( r_i \) is the coordinate of an atom, \( F_i \) is the composition of forces acting on atom \( i \) from the atoms surrounding atom \( i \). In molecular dynamics method, there is
\[ F_i = -\frac{\partial V}{\partial r_i} \]  

(2)

\( V \) is potential function among atoms. In order to obtain the movement of atoms, kinds of finite difference algorithm can be used.

Common algorithms are: Verlet algorithm, Beeman algorithm and Leapfrog algorithm. The research object of molecular dynamics is multi-particle system. The number of particles in system which can be simulated is finite because of the impact of external conditions. But the rule of statistical physics is still tenable, so suitable ensemble should be selected when simulating.

The master ensembles used in molecular simulation are Microcanonical Ensemble (NVE), Canonical Ensemble (NVT), Isobaric-isothermal Ensemble (NPT) and Pressure-enthalpy Ensemble (NPH). NVT is adopted in simulation in this article.

Particle number, volume, temperature and total momentum is conservation in NVT. The total energy of a system is not a conserved quantum at a constant temperature. Energy exchange must be occurred between the system and the external to maintain the temperature unchanged. The adopted method usually makes the heat balance between the system and the heat bath of external. A variable which bewrite the interaction between the system and the external is imported. Then Eq.(1) is changed into

\[ \dot{r} = \frac{F_i}{m} - \eta \dot{r}_i \]  

(3)

Where

\[ \eta = \frac{1}{\tau^2} (\frac{T}{T_c} - 1) \quad \tau = \frac{Q}{3Nk_B T_c} \]

\( \tau \) is the relaxation time of hot bath, determining the rate of tending to constant of system temperature, which can be evaluated equal or several times as time step. \( k_B = 1.3806 \times 10^{-23} \) J/K is Boltzmann constant.

The main numerical solutions of molecular kinetic equation are Verlet algorithm, Beeman algorithm and Leapfrog algorithm. The most extensively used Verlet algorithm is adopted in this article.

Suppose the positions of atoms in molecular system \( r(t) \) when the time is \( t \), then the positions of atoms can be obtained by Taylor expansion when the time is \( t + \delta t \)

\[ r(t + \delta t) = r_i(t) + \delta tv_i(t) + \frac{1}{2} \delta t^2 a_i(t) + \cdots \]  

(4)

and when time is \( t - \delta t \), there has

\[ r(t - \delta t) = r_i(t) - \delta tv_i(t) + \frac{1}{2} \delta t^2 a_i(t) - \cdots \]  

(5)

The Eq.(6) can be gotten by adding the Eq.(4) and Eq.(5)

\[ r(t + \delta t) = r(t - \delta t) + \delta t \frac{F_i(t)}{m_i} \]  

(6)

and then

\[ \nu(t) = \frac{[r(t + \delta t) - r(t - \delta t)]}{2\delta t} \]  

(7)

Because models are made of carbon nanotube and polyethylene, there are only C and H atom. Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential aiming at C and H atom is adopted in this article. The function between carbon nanotube and polyethylene is simulated by Lennard-Jones pair potential.

AIREBO potential\(^{[1]}\) can be written into

\[ E = \frac{1}{2} \sum_i \sum_{j \neq i} [E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} E_{ijkl}^{TORSION}] \]  

(8)
$E_{ij}^{REBO}$ gives the model its reactive capabilities and only describes short-ranged C–C, C–H and H–H interactions ($r < 2 \text{Å}$); $E_{ij}^{LR}$ adds longer-ranged interactions ($2 \text{Å} < r < r_{cut}$) using a form similar to the standard Lennard-Jones potential. $E_{ij}^{\text{TORSION}}$ is an explicit 4–body potential that describes various dihedral angle preferences in hydrocarbon configurations. Lennard-Jones potential can be written into

$$E = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \quad r < r_{cut} \quad (9)$$

Different parameters are given to $\varepsilon$ and $\sigma$ according to different atoms in the formula above.

### 3. procedure and result of simulation

In the simulation, carbon nanotube is supposed to be rigid material, which is distortion would not happen in the process of simulation. AIREBO potential is adopted in carbon nanotube and polyethylene, and the function between carbon nanotube and polyethylene is simulated by Lennard-Jones pair potential. The whole system adopts NVT ensemble and Nose-Hoover method is used to control the temperature at absolute zero, which avoided the influence brought by thermal activation. Verlet algorithm is used to solve molecular dynamics equations in the procedure of simulation. First, model will relaxed in 10000 time steps, so the energy is the smallest. Give a displacement of 0.01nm to carbon nanotube along to the direction of length. Relax 1000 time steps, and the time is $10^{-16}$ s. This will circulate until the carbon nanotube is divorced from polyethylene.

Figure 2 is the deformation of composite. From it we can see that some polyethylene chains will move along with carbon nanotube and the polyethylene chains that are far from carbon nanotube will keep the position when the displacement is small enough. Polyethylene chains will move slowly because of the increase of the displacement of carbon nanotube and the function of the immovable polyethylene chains. Last carbon nanotube divorces from polyethylene.

![Figure 2](image_url)

**Figure 2.** Deformation of composite

Figure 3 expresses the relationship of average potential energy and displacement of carbon nanotube. The potential energy arrives at minimum when the displacement is 0.35nm, as shown in Figure 2(b), because that the deformation of polyethylene is not obvious. From Figure 2., we can see that when the displacement in 0.35nm-0.62nm, carbon nanotube connects closely with polyethylene and mean stress of carbon nanotube achieves maximum along the direction of displacement. As the
displacement increases, the distance between carbon nanotube and polyethylene augments and mean stress decreases. It is shown as in the figure 4.

In the program used in this article, mean stress can be expressed as

\[
S_{ab} = -\left( m v_a v_b + \frac{1}{2} \sum_{n=1}^{N_p} (r_{i_a} F_{1b} + r_{i_b} F_{2a}) + \frac{1}{2} \sum_{n=1}^{N_p} (r_{i_a} F_{1b} + r_{i_b} F_{2a}) + \frac{1}{3} \sum_{n=1}^{N_p} (r_{i_a} F_{1b} + r_{i_b} F_{2a} + r_{i_b} F_{3b}) + \right.
\]

\[
\left. \frac{1}{4} \sum_{n=1}^{N_p} (r_{i_a} F_{1b} + r_{i_b} F_{2a} + r_{i_b} F_{3b} + r_{i_b} F_{4b}) \right) + \frac{1}{4} \sum_{n=1}^{N_p} (r_{i_a} F_{1b} + r_{i_b} F_{2a} + r_{i_b} F_{3b} + r_{i_b} F_{4b}) + \sum_{n=1}^{N_p} r_{i_n} F_{i_n}) \right]
\]  

(10)

The first term is a kinetic energy contribution for atom \( i \). The second term is a pairwise energy contribution where \( n \) loops over the \( N_p \) neighbors of atom \( i \), \( r_1 \) and \( r_2 \) are the positions of the two atoms in the pairwise interaction, and \( F_1 \) and \( F_2 \) are the forces on the two atoms resulting from the pairwise interaction. The third term is a bond contribution of similar form for the \( N_b \) bonds which atom \( i \) is part of. There are similar terms for the \( N_a \) angle, \( N_d \) dihedral, and \( N_i \) improper interactions atom \( i \) is part of. Finally, there is a term for the \( N_f \) fixes that apply internal constraint forces to atom \( i \).

Stress in Eq.(10) is the stress of every atom. Mean stress is the average of sum of stresses of all the atoms, it can be obtained by

\[
P = \frac{N k_B T}{V} + \frac{\sum_i r_i \cdot f_i}{dV}
\]  

(11)

The maximal mean stress can be computed out from the program when the displacement is 0.62nm. The numerical value is 17159.4MPa.

In continuum mechanics, there has \( F = \sigma A \), and \( A = 2\pi rl \). The maximum force of the carbon nanotube is \( 4.994 \times 10^{-7} \) N when the displacement is 0.62nm.

The interaction between carbon nanotube and polymer is the most obvious when displacement force is 0.35nm-0.62nm and then carbon nanotube gradually divorces from polyethylene.

**Figure 3.** displacement- average potential energy curve  
**Figure 4.** displacement-mean stress curve

### 4. Conclusion

The process of pulling out of the carbon nanotube from polyethylene was simulated by inlaying the carbon nanotube into polyethylene in Materials Studio and using a molecular dynamics program. The results showing the relationship of load displacement versus average potential energy and mean stress are obtained. Average potential energy reduces with the increase of displacement and then gradually
increases at a specific displacement. Axial force of the carbon nanotube was obtained at different displacement. The interaction between the carbon nanotube and polyethylene when pulling out and the potential changes of the carbon nanotube are obtained. The mechanical properties of polymer matrix composite materials are obtained on atomic scale.

References
[1] Ajayan P M, Stephan O, Collies C, Trauth D. Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. 1994, Science, 265:1212-1214.
[2] Schadler L S, Giannaris S C, Ajayan P M. Load transfer in carbon nanotube epoxy composites. 1998, App l Phys Lett, 73 (26):3842-3844.
[3] Cooper C A, Young R J, Halsall M. Investigation into the deformation of carbon nanotubes and their composites through the use of Raman spectroscopy. 2001, Composites: PartA, 32 (3-4):401-411.
[4] Biercuk M J, Llaguno M C, Radosavljevic M. Carbon nanotube composites for thermal management. 2002, Applied Physics Letters, 80(15):2767-2769.
[5] Wei C, Srivastava D, Cho K. Thermal expansion and diffusion coefficients of carbon nanotube-polymer composites. 2002, Nano Letters, 2(6):647-650.
[6] Dalton A B, Ferraris J P, Baughman R H. Continuous carbon nanotube composite fibers: properties, potential applications, and problems. 2004, J. Mater. Chem, 14:1-4.
[7] Lei Z K, Qiu W, Li Q, Kang Y H, Pan X M. Mechanical Properties of Carbon Nanotube Polymer Composites. 2008, Polymer Materials Science & Engineering, 12(24):134-140.
[8] Sharon K Pregler a, Byeong-Woo Jeong, Susan B Sinnott. Ar beam modification of nanotube based composites using molecular dynamics simulations. 2008, Composites Science and Technology, 68: 2049–2055.
[9] Zheng Qingbin, Xia Dan, Xue Qingzhong, Yan Keyou, Gao Xili, Li Qun. Computational analysis of effect of modification on the interfacial characteristics of a carbon nanotube/ polyethylene composite system. 2009, Applied Surface Science, 255, 3534–3543.
[10] Zhang Y, Gu J H, Shang J X, Ma Y. The base of computational materials science. 2007, Beijing University of Aeronautics and Astronautics Press.
[11] Fan J H. Multiscale analysis for deformation and failure of materials. 2008, Science Press.