

Molecular Dynamics Simulation of Carbon Nanotube Composites

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論文内容要旨

The discovery of carbon nanotubes (CNTs) has given a new dimension to nanocomposite research. CNTs represent an interesting class of nanostructure that can be described as a graphite sheet rolled into a seamless cylindrical shape. CNTs possess a combination of properties never seen before in a conventional material. CNTs can be seen as dream materials due to their high Young's modulus and tensile strength. High-strength CNTs have a potential application as reinforcing elements in composites, especially polymer-matrix composites, where the matrix tensile strength is very low (on the order of 200 MPa). CNT can also be used at the interface of the macroscopic carbon fiber reinforced polymer (CFRP) composites to increase the strength of the CFRP composites. During the fiber break or interfacial debonding in macroscopic polymer composites, CNTs at the interface could bridge the cracks or pull-out at the fractured regions. This improves the interfacial strength and toughness in macroscopic composites. The interfacial strength of the CNT-polymer at the interface will affect that of the CFRP composites. Since the load-transfer properties represent the main factor in ensuring that the composite system is functioning properly, investigation of the interfacial strength between embedded CNTs and matrix is important.

Since interfacial shear strength (ISS) of the CNT-polymer composite has a great influence on the strength and interfacial toughness of the polymer composites, it is necessary to improve the ISS of CNT-polymer system. Therefore, it is important to investigate the effects of different factors (i.e. simulation and experimental conditions) on the ISS or how ISS of the CNT-polymer composites can be increased. Due to the difficulties associated with nanoscale size of the CNTs, there are few experimental works, which characterize the interfacial strength of the CNT-polymer composites. All the experimental measurements are indirect and there is no accurate information as to the magnitude of the ISS. There are also some molecular simulations studies characterizing the ISS of the CNT-polymer composites. In the molecular simulations, considering detailed structure (i.e. C-C and C-H bond) of the polymer chains is computationally much expensive. For instance, to reduce the computational time some researchers have considered small displacement of the nanotubes, which could not discuss the interfacial failure. To reduce the computational time some other researchers did not consider the deformation of the polymer matrix. Thus, they assumed rigid polymer matrix in their simulations. To overcome these limitations in the computational works, an efficient simulation scheme is necessary.

This study introduces an efficient simulation scheme in sense of computational time by modeling both the polymer matrix and cross-links with a united-atom potential. In the united-atom approach, detailed structures (i.e. C-H and C-C bond) of the

polymer chains are not considered. Rather polymer chains are represented by a set of united-atom. Each united-atom corresponds to a monomer (i.e. repeating unit) of the polymer. Thus this approach enables us to simulate a large-scale model with less computational time than conventional approach. Since united-atom approach does not consider the detailed structure of the polymer, switching of the cross-link chains at the interface will not occur automatically during relative movement between the nanotubes and the polymer matrix. Special methodology is required for cross-link switching when united-atom approach is adopted. This study introduces a new switching criterion for the cross-links based on minimum energy. Therefore, this study enables us to characterize the interfacial properties of large CNT-polymer system considering interfacial failure. Using our simulation scheme we investigate how the ISS can be increased and what factors influence the ISS of the CNT-polymer composite. In this thesis, the effects of the following factors on the ISS of the CNT-polymer composite are examined.

1. Polymer matrix density
2. Chemical cross-links at the interface between the CNT and the polymer matrix
3. Geometrical defects in the CNT
4. Atomic defects in the CNT
5. Edge effect of the CNT.

In this study, ISS of the CNT reinforced polyethylene composite is investigated by CNT pull-out using molecular dynamics simulations. Classical molecular dynamics is used where Newtonian equations of motion are solved numerically using the velocity-Verlet algorithm for a set of atoms. We use classical molecular dynamics since it is simple and takes less computational time compared to the quantum molecular dynamics. In the simulations, crystalline polyethylene is considered as polymer matrix. Carbon-carbon interactions in the CNT are modeled by the Brenner potential and the polyethylene polymer is modeled by a united-atom potential. Each $-\text{CH}_2-$ group is considered as a single atom in the united-atom approach. Therefore, for the same size model, united-atom approach reduces the number of the atoms by two third since three atoms (i.e. one carbon atom and two hydrogen atoms) of the $-\text{CH}_2-$ group are represented by one atom. Due to this reduction in the number of atoms, computational time is hugely reduced. For example, for a simulation model with two $-\text{CH}_2-$ groups, united-atom approach will save approximately ten times computational time.

A simple physical model of the CNT-polymer is considered in this study where a single-walled CNT is partially embedded into the polymer matrix. Though this model is simple, it is meaningful. The reason behind this, in real CNT based polymer composites short length CNTs are pulled out from the surrounding matrix in the fractured regions. Therefore, to investigate the nanoscale interfacial properties of CNT based polymer composites such model will work well. Moreover, plastic deformation of the interface is neglected considering only crystalline polymer as the matrix. ISS is calculated based on energy balance criterion given by Eq. (1), where energy difference of the CNT-polymer system in the pull-out process is considered as the total work done of the pull-out.

$$W = \pi r_f \tau_i L_e^2. \quad (1)$$

In Eq. (1), W is the pull-out work (i.e. energy), r_f is the CNT radius, L_e is the CNT embedded length, and τ_i is the ISS.

Interface is modeled with and without the presence of polyethylene cross-links. Cross-links connect the CNT with the surrounding polymer matrix. For the first time, polymer cross-links in the CNT-polymer composite interface is also modeled

by the united-atom potential. During the pull-out of the CNT with cross-links at the interface, cross-link may completely detach from the CNT or it may switch from one position to another position on the CNT. However, since our simulation, based on the united-atom approach, does not address the chemical bond of C-H and C-C in the polymer, the switching phenomena between the CNT and the cross-link cannot be simulated automatically. Then, we introduce a new switching criterion here based on minimum energy. This energy is the total of the bond stretching, bond bending, bond torsion, and nonbonded van der Waals energies of the cross-link. The relative energies of the cross-link are calculated at different positions around the present position after the calculation of its motion. The cross-link end atom moves to a new position if the new position gives a lower energy. If the cross-link end bond length exceeds or becomes equal to the bond-breaking length then cross-link may detach from the CNT or switch to another position on the CNT.

Cross-link connects the CNT with the polymer matrix by coinciding its one end atom with a polymer matrix atom, and the other end atom with a CNT atom. Figure 1 illustrates schematic of a CNT with one polymer matrix chain and one cross-link chain of four atoms.

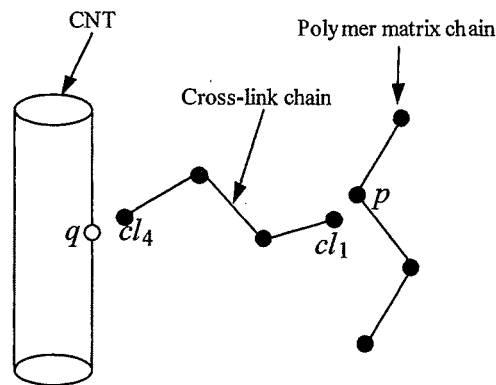


Fig. 1 Schematic of CNT along with a polymer matrix chain and a cross-link chain.

Force calculation procedures for the coincident CNT and polymer atoms are described below. It is assumed that atom p in the polymer matrix coincides with cross-link atom cl_1 and that atom q in the CNT coincides with cross-link atom cl_4 . The force of atom q is then calculated as follows:

Step 1. Calculate the force of atom q considering the CNT-polymer system without the cross-link.

Step 2. Calculate the force of atom cl_4 considering only the cross-link.

The total force of atom q is the sum of the forces calculated in Steps 1 and 2. The total force of atom p is calculated using the similar procedure. The new positions of atoms p and q are then calculated by solving the Newtonian equations of motion. We assumed that atom cl_1 always coincides with atom p . However, atom cl_4 may coincide with another CNT atom based on the minimum energy criterion. Our simulation approach cannot discuss the automatic switching of the cross-links. However, it can discuss the deformation phenomena for the cross-links taking less computational time.

The thesis consists of five chapters. Chapter 1 is the introduction. Here details about CNTs, their applications in composite materials, literatures review regarding the interfacial strength of the CNT-polymer composites, and objectives of this work are discussed. In Chapter 2, effects of polymer matrix density, cross-link at the interface, and geometrical defects are examined. Details about the different empirical potential functions, atomistic simulation model, and simulation conditions are discussed in this chapter. In the simulation, the crystalline polyethylene matrix is set up in a hexagonal array with the polymer chains

parallel to the CNT axis. Matrix densities are adjusted by changing the distance between the polymer chains. For geometrical defects, two pairs of pentagons and heptagons are inserted at the same location, also called a 5-7-7-5 Stone-Wales defect. In this defect, four neighboring hexagons convert into two pentagons and two heptagons with a 90° rotation of a horizontal bond of the hexagonal structure. Validity of the potential functions is also discussed in this chapter. From the simulated results of CNT pull-out from polymer, the following conclusions for the effects of matrix density, chemical cross-links and geometrical defect of CNT on the ISS of the CNT-polymer composite are obtained.

- Matrix density affects the ISS of the CNT reinforced polymer composite. It is found that with the increase of matrix density ISS increases.
- Presence of chemical cross-links at the interface increases the ISS of the CNT-polymer composite.
- Cross-link position affects the ISS. Cross-links having smaller traveling distance give relatively higher ISS though in that case energy is transferred for smaller pull-out displacement.
- Pentagon-heptagon geometrical defects do not affect the ISS when there are no cross-links at the interface. However, they reduce the ISS when cross-links are present at the interface.

In Chapter 3, effects of CNT vacancy defects (i.e. missing atoms) on the ISS of the CNT-polyethylene composite are investigated. Three patterns of vacancy defects: one-atom vacancy, two-atom vacancy and vacancy at the same ring are considered. CNT pull-out simulations from the polymer matrix are conducted considering two types of interfaces, with and without polyethylene cross-links between the CNT and the matrix. Tensile tests of the CNT are also conducted with the same types of vacancy defects for examining their effects on the CNT tensile strength. Details of the CNT tensile test procedure are discussed in this chapter. From the simulated results the following conclusions are obtained.

- When vacancy defect sites are distributed at different positions in the CNT, tensile strength of the CNT is not significantly affected by the increase of vacancy defects. However, tensile strength decreases with the increase of vacancy defects when they accumulate at the same ring of the CNT.
- ISS decreases as the vacancy defects increase.
- For the same number of missing atoms, one- and two-atom vacancy defects do not affect the ISS when there is no cross-link at the interface. However, they do affect the ISS when there are cross-links at the interface.
- For the interface with cross-links, when vacancy defects accumulate at the same ring of the CNT, CNT fails during the pull-out process. This fracture significantly reduces the ISS.

Chapter 4 investigates the effects of the CNT end conditions on the ISS of the CNT-polyethylene composite. CNT pull-out from the polymer matrix are conducted considering two types of interfaces, with and without polyethylene cross-links between the CNT and the matrix. End conditions effects are investigated considering open-end CNT (i.e. CNT without cap) and capped CNT. Two types of caps, pencil cap, and buckyball cap are considered for capped CNT. From the simulated results the following conclusions are obtained.

- CNT end conditions have negligible effects on the ISS of the CNT-polymer composite when there are no cross-links at the interface. It may be due to the flexible geometrical constraints of the CNT in the CNT-polymer composite.
- ISS is significantly affected by the CNT end conditions when there are cross-links at the interface of the CNT-polymer composite.

Chapter 5 summarizes the main results of this study.

論文審査結果の要旨

カーボンナノチューブは高剛性、高強度を有する次世代材料として期待がかけられている。特に、航空宇宙構造の主要な構造材料となりつつある繊維強化プラスチック複合材料においては、繊維・マトリックス界面にカーボンナノチューブを配置することで、界面特性を改善しようという試みが数多くなされている。この界面特性を改善する上での重要な因子は、母材であるプラスチックからのカーボンナノチューブの引抜け特性である。しかしながら、この特性評価においては、原子レベルにおける変形・破壊について議論が必要なため、実験による検証は数えるほどしかない。また、数値解析による研究も、今のところ比較的小さな系を対象に行われているのみで、現象を明確に解明するには至っていない。

本論文は、プラスチック中に埋め込まれたカーボンナノチューブの引抜け特性を、効率良く解析する分子動力学手法を提案し、本解析法をもとにカーボンナノチューブ中の欠陥および形状が引抜け特性に及ぼす影響について検証した研究であり、全編5章からなる。

第1章は序論である。

第2章は、分子モデルを用いたプラスチックおよびカーボンナノチューブの両方を考慮した分子動力学シミュレーションにおける新しい解析手法を提案している。この手法により、従来に比べて大きな系を対象とした計算を行うことが可能となり、特に、界面間における化学結合状態をエネルギーの観点から決定する結合遷移解析手法は、計算効率の観点において画期的な手法である。得られた解析結果はすべてを原子ポテンシャルにて扱った大規模な数値計算結果と整合し、妥当なものである。これは工学上極めて有益な成果である。

第3章は、第2章で提案した分子モデルを用いた新しい解析手法を、原子レベルでの欠陥を有するカーボンナノチューブのプラスチックからの引抜け特性解析に適用したもので、原子レベルでの欠陥が引抜けに大きな影響を与えることを明らかにした。これは、カーボンナノチューブを利用し繊維強化プラスチック複合材料の界面特性を改善する上で、極めて有益な知見である。

第4章は、カーボンナノチューブ端部の幾何形状がプラスチックからの引抜け特性に及ぼす影響を、詳細に検証している。このような数値解析による検証は、計算負荷が極めて大きいため過去に例がなく、本論文において提案した解析手法により初めて可能となったものであり、新規性に優れた重要な成果である。

第5章は結論である。

以上要するに本論文は、母材であるプラスチックからのカーボンナノチューブの引抜け特性をプラスチックおよびカーボンナノチューブの両方を考慮したうえで、効率良く解析する手法を提案したものであり、航空宇宙工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。