

# Influence of Inter-tube Connections on the Stress-Strain Behavior of Nanotube-Polymer Composites: Molecular Dynamics

Jianwei Zhang\*, Dazhi Jiang, Huaxin Peng, Chunqi Wang

**Abstract**—Stress-strain curve of inter-tube connected carbon nanotube (CNT) reinforced polymer composite under axial loading generated from molecular dynamics simulation is presented. Comparison of the response to axial mechanical loading between this composite system with composite systems reinforced by long, continuous CNTs (replicated via periodic boundary conditions) and short, discontinuous CNTs has been made. Simulation results showed that the inter-tube connection improved the mechanical properties of short discontinuous CNTs dramatically. Though still weaker than long CNT/polymer composite, more remarkable increase in the stiffness relative to the polymer was observed in the inter-tube connected CNT/polymer composite than in the discontinuous CNT/polymer composite. The manually introduced bridge break process resulted in a stress-strain curve of ductile fracture mode, which is consistent with the experimental result.

**Keywords**—Carbon nanotube, inter-tube connection, molecular dynamics, stress-strain curve

## I. INTRODUCTION

SINCE their discovery [1], carbon nanotubes (CNTs) have attracted the attention of many scientists and engineers worldwide, owing to their outstanding mechanical, thermal and electrical properties [2-4]. The combination of low density, nano-scale diameter, high aspect ratio, and more importantly, extremely high mechanical strength and modulus, makes CNTs an ideal reinforcing filler for polymer composites with excellent performance [3-5]. However, their performance in reinforcing polymer matrices so far has been inadequate, which was attributed by researchers to several challenges, including: (a) homogeneous dispersion or alignment of CNTs in the matrix, and (b) strong interfacial interactions to ensure efficient load transfer from the polymer matrix to the CNTs. In order to obtain desirable CNT/polymer composites, several methods such as chemical functionalization [6-8], polymer wrapping [9], plasma treatment [10] have been applied to modify the CNT surfaces.

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The surface modification is known to promote the dispersion of CNTs in the polymer matrix and increase the CNT-polymer interfacial interactions. But these techniques still don't take full advantage of the superior mechanical properties of CNTs. Zhang and Jiang [11] developed a novel approach to further exploit the mechanical properties of CNTs by interconnecting CNTs via chemical functionalization. The chemical interconnection process improved the toughness of the CNT/polymer composites significantly.

However, due to the technical difficulties in conducting direct investigation, the micro mechanical mechanisms of inter-tube CNT connections on the bulk mechanical properties of the composites still remained unclear. Molecular dynamics (MD) simulation has been selected as an effective method to characterize the mechanical properties and understand the micro mechanisms of deformation. Various aspects of the mechanical reinforcement of CNT/polymer composites, such as tube-matrix interfacial bonding [12], sidewall functionalization [13], concentration of matrix [14], have been addressed computationally by researchers. Bulk mechanical properties of both CNTs and CNT/polymer composites were also predicted by investigating the stress-strain curves generated from MD simulations [15-16]. All these results have shown an encouraging path toward MD simulation application in studying the mechanical properties of CNT/polymer composites.

The objective of this study is to explore the effects of inter-tube chemical connections on the overall mechanical properties of unidirectional CNT/polymer composites using MD simulation method. The overall mechanical properties of CNT/polymer composites were provided by the stress-strain relationship generated from MD simulations. In the present study, stress-strain curves of unidirectional CNT/polymer composite systems under axial loading were demonstrated by examining three different configurations, which contained continuous (infinitely long) CNTs, short, discontinuous CNTs and interconnected short (semi-continuous) CNTs, respectively. Stress-strain curves of the three different configurations of CNTs without matrix were also generated for comparison.

## II. EXPERIMENTAL

### A. MD Simulation Models

The unidirectional CNT/polymer composite systems established in this work contained symmetrically placed infinitely long or short (both discontinuous and linked) CNTs, as shown in Fig. 1. In each system, the CNTs (represented by the dark area) are sufficiently separated by polymer matrix (represented by the white area) to prevent direct CNT wall-wall interactions. All the CNTs built for simulations are (10, 10) CNTs, while the long continuous CNTs are periodically

replicated, and the unsaturated boundary effect of short discontinuous CNTs was avoided by adding hydrogen atoms at each ends. In Fig. 1c, the neighboring short CNTs are chemically linked (end to end), as shown in detail in Fig. 2. The stable crosslink can be formed by two carboxyl groups on neighboring CNTs [17]. The gray balls represent carbon atoms, the white balls represent hydrogen atoms, and the red balls represent oxygen atoms. An amorphous polyethylene (PE) matrix, with chains of 200  $-\text{CH}_2-$  units and a density of  $0.90 \text{ g/cm}^3$ , was used. In each composite lattice, the PE matrix contains 38 chains of  $-\text{CH}_2-$  units. The dashed boxes in Fig. 1, with dimension of approximately  $50 \times 50 \times 100 \text{ \AA}$ , enclose a representative volume element that is simulated by MD method. The lattice length was approximately the same as that of the short CNT. Periodic boundary conditions were used to replicate the lattice in all three dimensions.

For comparison, equivalent-sized blocks of pure amorphous PE system without CNTs (with 42 chains of  $-\text{CH}_2-$  units) and neat CNT systems without PE matrix were also simulated.

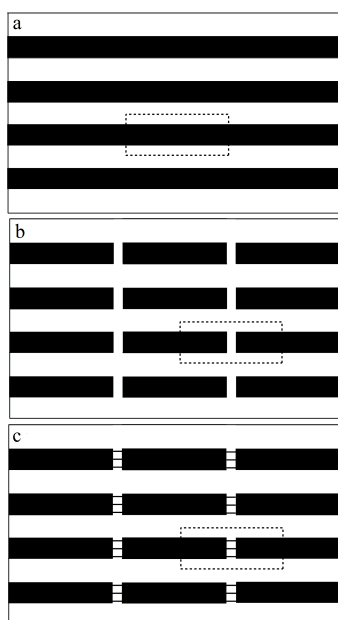


Fig. 1 Schematic of CNT/polymer composite system filled with (a) long, (b) short discontinuous, (c) covalently linked short CNTs

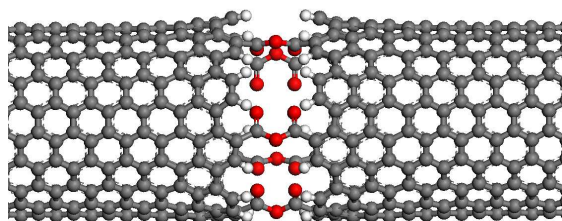


Fig. 2 Atomic model of the carboxyl bridges formed between neighboring CNTs

### B. MD Simulation Force-field

The MD simulations were carried out by using Materials Studio<sup>®</sup>, a commercial software package developed by Accelrys Inc. The condensed phase optimized molecular potentials for atomistic simulation studies (COMPASS) force-field was used to conduct computations [18]. Previous successful researches on the CNT/polymer composite systems using the COMPASS force-field have been reported [19-22]. All simulations in the present study were carried out at 300 K with a 1 fs ( $1 \times 10^{-15}$  s) time step, using constant number of particles, constant volume and constant temperature (NVT) ensembles.

### C. Stress-strain Curves from MD Simulation

#### 1. Strain

For each increment of applied axial deformation, a uniform strain was prescribed on the entire MD model. The application of strain was accomplished by uniformly expanding the dimensions of the simulation lattice in the axial direction [16]. The new coordinates of the atoms were re-scaled by keeping their fractional coordinates fixed during the lattice expansion. After each deformation of 1% increment of strain, MD simulation was carried out and the atoms were allowed to equilibrate within the new MD lattice dimensions. This process included two steps: the system was relaxed for  $1 \times 10^3$  steps first, and then total energy of the system was average over an interval of  $1 \times 10^4$  steps. For each system, twenty increments of 1% strain were applied, up to a total deformation of approximately 20%. The corresponding strain rate was about  $1.0 \times 10^{10} \text{ s}^{-1}$ . This strain rate is extremely high for the MD simulations are usually on ps ( $1 \times 10^{-12}$  s) or ns ( $1 \times 10^{-9}$  s) timescales.

#### 2. Stress

In this paper, the stress was calculated by directly computing the change of internal energy with respect to the strain per unit volume under each deformation mode [23]. At the continuum level, the stress tensor,  $\sigma$ , for a linear-elastic material is:

$$\sigma = \frac{1}{V_0} \left( \frac{\partial E}{\partial \varepsilon} \right)_S \quad (1)$$

where  $V_0$  is the initial volume of the system,  $E$  is the total internal energy,  $\varepsilon$  is the strain tensor, and the subscript  $S$  denotes constant entropy. For a CNT system,  $V_0$  is given by  $V_0 = 2\pi r h L$ , where  $L$  is the length,  $r$  is the radius, and  $h$  is the equivalent tube wall thickness taken as  $0.617 \text{ \AA}$  [15] in this paper. The internal energy is the sum of bonding energy and nonbonding energy. For the CNT/polymer system, the nonbonding term is mainly the energy of van-der-Waals force.

### III. RESULTS AND DISCUSSION

The stress-strain curves of (a) neat CNT systems, including long CNTs, separated short CNTs and linked short CNTs, (b) pure polymer and short CNT/polymer composite systems, and (c) long and linked short CNT/polymer composite systems

generated from MD simulations are presented in Fig. 3. It should be noted that the curves are from 1% strain points and the endpoints are indicative of how far the simulations were conducted, and should not be taken as yield points. For all the neat CNT or composite systems, the maximum strains are on the order of 20% after the unit lattice has been subjected to the stepwise increments of applied strain. The strain leads to an overall strain of approximately 2.0 nm for each unit lattice in the axial direction. No bond broken was taken into account except for that introduced manually in the linker broken short CNT/polymer composite system, and hence the stress-strain curves are all approximately linear.

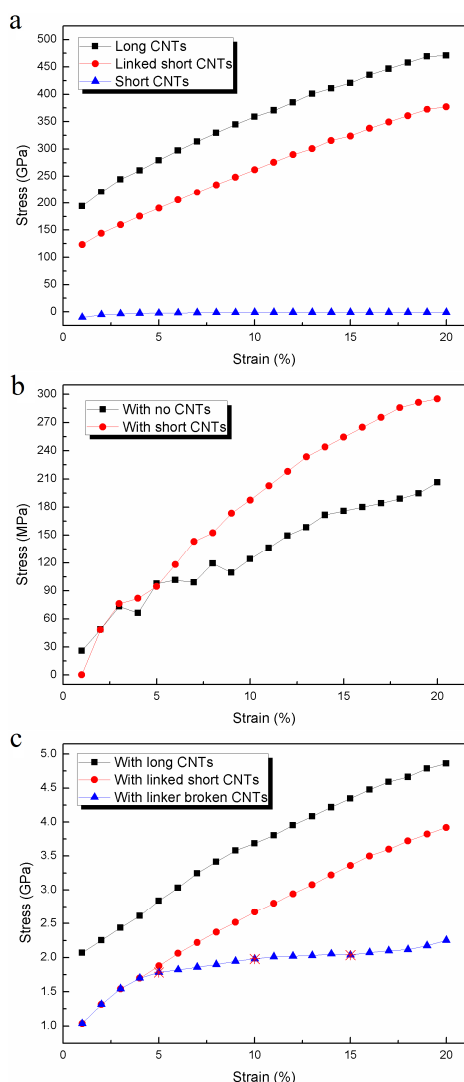


Fig. 3 Atomic model of the carboxyl bridges formed between neighboring CNTs

It can be seen in Fig. 3a that, the modulus for the separated short CNTs is almost zero for there are only weak nonbonding tube interactions between them, while the inter-tube carboxyl bridges increase the modulus dramatically. The bridges can transfer stress between neighboring CNTs effectively.

It can also be seen that the modulus of the infinitely long CNTs is much higher than that of the covalently linked short CNTs, for the overall mechanical properties of the CNTs are strongly depended on the weakest section (carboxyl bridges) of the tube. Enhancement of the stiffness relative to the neat polymer is observed in the stress-strain curve of the composites with embedded 10 nm short CNTs in Fig. 3b. This effect is consistent with the strong interfacial interaction between the CNTs and polymer matrix. In another sense, though the volume fraction of the short CNTs in the composites is quite high (about 6%), the polymer stiffness is not improved proportionately as in the long CNT/polymer composites. The main reason is the low aspect ratio (about 7:1) of the short CNTs. Comparatively, the improvement of stiffness of composites reinforced by the long CNTs with infinitely high aspect ratio is quite higher than that of the separated short CNTs, as shown in Fig. 3c. The curvature of stress-strain curves of the composites embedded with long CNTs and linked short CNTs in Fig. 3c are similar to that of the neat long CNTs and linked short CNTs in Fig. 3a. The reason for this behavior is that the infinitely long CNTs and linked short CNTs acted as continuous reinforcing fibers, and the modulus of the composites is mainly controlled by the modulus of the strong “fibers” following the “rule of mixtures”.

During the MD simulation, it was found that the carboxyl bridges in the linked short CNTs are the stress concentration locations. It indicated that the carboxyl bridges are much easier to break while the composites are under axial strain loading. To represent the mechanical behavior much closer to reality, break of carboxyl bridges were introduced manually. At the strain of 5%, 10% and 15%, one, two and three of the five carboxyl bridges were broke stepwise. The stress-strain curve of the linker broken CNT/polymer composites is also shown in Fig. 3c. This curve shows a mode of ductile fracture, which is consistent with the experimental results obtained by Zhang [11]. The curves also show that, with the numbers of broke linker increasing, the modulus of the composite decreases and gets more and more closer to the modulus of the polymer reinforced by separated short CNTs. It suggest a reinforcing mechanism for the inter-tube connected CNTs. While under loading, the interconnected CNTs were elongated by the interfacial stress, and the deformation of CNTs finally results in the break of the tube bridges, which consumes plenty of energy. This will hinder the propagation of cracks or CNT-polymer interface delamination. This mechanism results in a toughness significantly improved composites, relative to the separated short CNT/polymer composites.

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