J Mater Sci (2009) 44:339–341
DOI 10.1007/s10853-008-3127-7

LETTER

Effect of cross-links on the pullout of carbon nanotubes from amorphous polymer

M. Nishikawa · T. Okabe · T. Honda

Received: 29 August 2008 / Accepted: 20 November 2008 / Published online: 14 December 2008
© Springer Science+Business Media, LLC 2008

The use of carbon nanotubes (CNTs) as fiber reinforcement in polymer matrix composites is currently being investigated because of their superior mechanical, electrical, and thermal properties [1]. However, recent research has raised some concerns that the widespread use of CNTs may lead to mesothelioma, cancer of the lining of the lungs, just like asbestos [2]. During the machining of the CNT-reinforced composites, CNTs may be pulled out of the polymer matrix and spewed into the air, where they present health risks. To ensure safety in using and manufacturing CNT-based products, a detailed understanding of the CNT pullout from a polymer matrix is essential.

The CNT pullout from a polymer matrix has been investigated with classical molecular dynamics simulations [3–5]. In addition to the nonbonded van der Waals interaction, the chemical bond (i.e., cross-link) between CNT and polymer matrix plays an important role in the pullout [5]. The pullout at nanoscale levels exhibits an interesting debonding–rebonding behavior of the cross-link. When the cross-link separates, there is a sudden drop in force, but this is followed by rejoining of the hydrocarbon chain with adjacent atoms of the CNT. The debonding–rebonding behavior greatly affects the resulting pullout force. Our previous work [6] presented a new approach addressing such interfacial molecular switching behavior of the cross-link for a CNT and crystalline-polymer system. An energy-based switching criterion was incorporated into a molecular dynamics simulation to deal with cross-links traveling on the CNT, without directly solving the many-body interaction between the CNT and polymer. With this molecular dynamics simulation, we investigated the effect of cross-link switching on the pullout of CNT from amorphous polymer in this study.

We will first explain the procedure of the molecular dynamics simulation. Figure 1 depicts the unit-cell model for the CNT-polyethylene (PE) system used in this study. The CNT was modeled as a graphite tube consisting of C atoms. The amorphous polymer chains were modeled by the united-atom model, which treats a CH_2 methylene group as a single united atom. Though the united atom model neglects the debonding and rebonding in polymer, it enables us to simulate a large system within a limited computational power. The axial length of the matrix was 6.0 nm and the model's cross-sectional area was 4.0×4.0 nm^2. The model included a (5,5) armchair CNT with an aspect ratio of 9.2 (530 atoms) at its center. The axial length of the CNT was 6.4 nm, and that of the CNT-embedded portion was approximately 5.5 nm. In order to reproduce the amorphous structure of the PE, chains of CH_2-united atoms were randomly located outside the CNT. The bond length r and bond angle θ were set to the equilibrium values; $r_0 = 0.153$ nm and $\theta_0 = 110.0°$. The dihedral angle ϕ was set to a random angle within 5° of the "gauche" angle (65°) or "trans" angle (180°) that gives the minimum energy of the dihedral angle potential. The separation distance between the nonbonded united atoms exceeded 0.25 nm. The chains were successively created until the PE density reached 1.0 g/cm^3. The model contains 212 chains with 20 CH_2-united atoms for each (i.e., 4240 CH_2-united-atoms).

M. Nishikawa
Department of Aeronautics and Astronautics, The University of Tokyo, c/o Transdisciplinary Sciences Bldg, 5-1-5 Kashiwanoha, Kashiwa-shi, Mailing Box 311, 277-8561 Chiba, Japan

T. Okabe (✉) · T. Honda
Department of Aerospace Engineering, Tohoku University, 6-6-01 Aoba-yama, Aoba-ku, 980-8579 Sendai, Japan
e-mail: okabe@plum.mech.tohoku.ac.jp

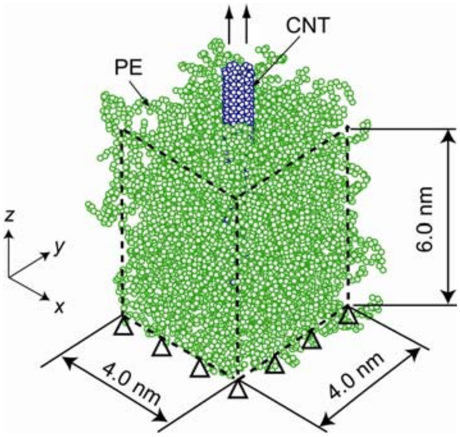

Fig. 1 Schematic of the atomistic model for the CNT pullout from amorphous PE

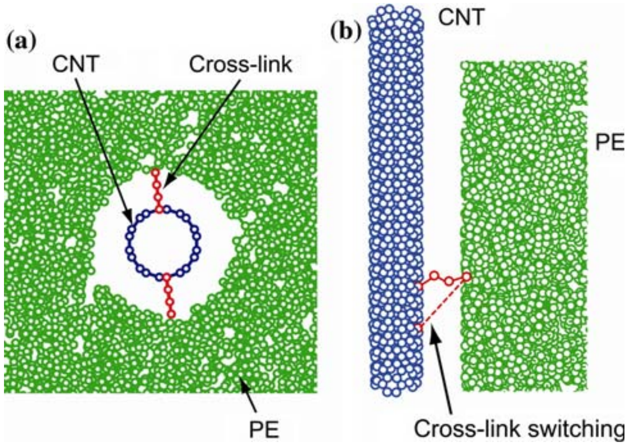

Fig. 2 Schematic of cross-links between the CNT and the polymer matrix

The total potential energy E of the system is composed of that of the CNT (E_{CNT}), that of the amorphous PE (E_{PE}), and that of the interface between CNT and PE matrix (E_{int}).

$$E = E_{\mathrm{CNT}} + E_{\mathrm{PE}} + E_{\mathrm{int}} \tag{1}$$

The Brenner potential [7], which is used for carbon–carbon interaction in the CNT, is given as

$$E_{\mathrm{CNT}} = \sum_i \sum_{j(>i)} \left\{ V_{\mathrm{R}}(r_{ij}) - \bar{B}_{ij} V_{\mathrm{A}}(r_{ij}) \right\}, \tag{2}$$

where r_{ij} is the bond length from atoms i to j. $V_{\mathrm{R}}(r_{ij})$, $V_{\mathrm{A}}(r_{ij})$, and $\bar{B}_{ij}$ denote pair-additive repulsive and attractive interactions, and a many-body coupling term, respectively. The second set of parameters given by Brenner [7] was adopted here. The following united-atom potential given by Capaldi et al. [8] was used for PE chains.

$$E_{\mathrm{PE}} = \sum \left\{ E_{\mathrm{bs}}(r) + E_{\mathrm{be}}(\theta) + E_{\mathrm{to}}(\phi) + E_{\mathrm{vw}}(\bar{r}) \right\}, \tag{3}$$

where E_{bs}, E_{be}, and E_{to} are the bond-stretch, bond-angle, and bond-torsion potential energies, respectively. E_{vw} is the van der Waals interaction energy that depends on the distance $\bar{r}$ between two nonbonded polymer united atoms.

The pull-out simulation was conducted with and without cross-links in the interface. With no cross-links, the nonbonded van der Waals interaction between the CNT and the polymer is modeled with the 12-6 Lennard-Jones potential, given as

$$E_{\mathrm{int}} = \sum 4\varepsilon \left\{ \left(\frac{\sigma}{\bar{r}}\right)^{12} - \left(\frac{\sigma}{\bar{r}}\right)^{6} \right\}, \tag{4}$$

where ε is the potential well depth and σ is the van der Waals separation distance. We adopted $\varepsilon = 0.4492$ kJ/mol and $\sigma = 0.3815$ nm [6], and set a cut-off radius of 1.0 nm.

For the interface with cross-links, the cross-link bonding was considered in addition to the van der Waals interaction of the interface. Cross-link chains, consisting of four united atoms, were added in the interface (Fig. 2a). The cross-link chain was modeled by the CH_2-united atom chain. Figure 2b schematically illustrates the cross-link chain. The cross-link switching was represented as the switching of the CNT atom to which the end atom of the cross-link was attached. This study employed an energy-based switching criterion [6]. When a new position gave a minimum energy, the cross-link end atom was attached to the new position as depicted in Fig. 2b. If the cross-link end bond length exceeded the bond-breaking length then cross-link detached from the CNT. The bond-breaking length was set to twice the equilibrium bond length of PE.

These cross-link chains were inserted into the interface after the total energy of the CNT-polymer system without cross-links was minimized by the relaxation for over 16.0 ps. The CNT pullout from an amorphous PE matrix was simulated using this initial configuration. Equations of motion were solved using the velocity-Verlet method with a time step of 0.5 fs. The temperature of the system was kept constant at 300 K and controlled by velocity scaling. The boundary conditions are schematically illustrated in Fig. 1. Four sides of the unit cell were subjected to periodic boundary conditions. The bottom end of the CNT was free, while an incremental displacement of 3.0×10^{-4} nm was applied to the atoms of the last three rings of the exposed end of the CNT. Each incremental end displacement was followed by the conjugate energy minimization method and eight molecular dynamics steps for equilibration of the system. The cross-link switching was judged every ten steps.

We present the results of molecular dynamics simulation for the CNT-polymer system without cross-links and with two, four, and six cross-links. The cross-links were arranged at the same cross section, which was near the center of CNT embedded length, as depicted in Fig. 1. Figure 3 compares the relation between the pullout displacement

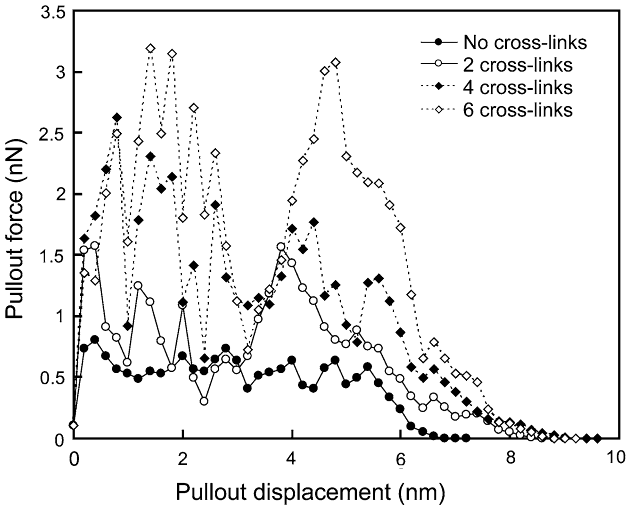

Fig. 3 Pullout force versus displacement when the number of cross-links is varied

and the total force applied to the CNT by the surrounding polymer.

With no cross-links, the pullout force peaks at 0.8 nN just after the pullout simulation starts. The resistible surface pressure, defined as the peak pullout force divided by the interfacial area between the CNT and the polymer (i.e., interfacial strength), is 66 MPa. This means that when that surface pressure is applied to the composite, the applied force, localized to the CNT in the region where the CNT sticks out of the polymer matrix, is likely to pull the CNT out of the matrix and into the air. In this case, the interfacial strength between the CNT and the polymer cannot adequately ensure the safety of using and manufacturing CNT-based products.

For interfaces with cross-links, multiple peaks appear in the relation between pullout force and displacement. As pointed out by Namilae and Chandra [4], the pullout force drops and rises successively due to cross-link switching. When the cross-link switches frequently, the pullout force continues to drop. The pullout force begins to rise while the motion of the polymer chain to which the crosslink is attached is restricted by other polymer chains and the chain of the cross-link is extended. The peak force is not necessarily reached in the initial stage of the pullout. As our previous study [6] reported, the interfacial shear strength increases as the PE density increases, so the variation of the pullout force may be controlled by the local density of the PE matrix. The local density of the polymer chains influence the restricted motion of the polymer chain to which the cross-link is attached and consequently influences the reaction force.

As the number of cross-links increases, the peak force increases as shown in Fig. 3. Even if cross-link switching is permitted to reduce the reaction force, the cross-link serves as the driving force to resist the external pullout force. The corresponding interfacial strength is then 130 MPa for two cross-links, 216 MPa for four cross-links, 263 MPa for six cross-links. Previous experiments using atomic force microscopy by Barber et al. [9, 10] reported the interfacial strength between the CNT and the polymer. In the case of no chemical bonding, the interfacial strength was 47 MPa between pristine CNT and PE-butene matrix and 30 ± 7 between pristine CNT and epoxy matrix. For chemically modified CNT, the interfacial strength increased up to 151 ± 18 MPa. The interfacial strength calculated with our simulation is very close to the order of those experimental values. From these discussions, we can conclude that the chemical bond between the CNT and the polymer significantly increases the resistible surface pressure. In the conventional composite materials with micro-fiber, the strong interface, such as the interface between carbon fiber and epoxy matrix, has 100 to 200 MPa strength [11, 12]. This interfacial strength can be achieved when the density of the cross-link per CNT atom reaches about 0.5 to 1%.

Acknowledgement T. O. acknowledges the New Energy and Industrial Technology Development Organization (NEDO) (Project No. P08024) for support.

References

1. Thostenson ET, Ren Z, Chou TW (2001) Compos Sci Technol 61:1899
2. Poland CA, Duffin R, Kinloch I, Maynard A, Wallace WAH, Seaton A, Stone V, Brown S, MacNee W, Donaldson K (2008) Nat Nanotechnol 3:423
3. Liao K, Li S (2001) Appl Phys Lett 79:4225
4. Namilae S, Chandra N (2005) J Eng Mater Technol 127:222
5. Al-Ostaz A, Pal G, Mantena PR, Cheng A (2008) J Mater Sci 43:164. doi:10.1007/s10853-007-2132-6
6. Chowdhury SC, Okabe T (2007) Composites A 38:747
7. Brenner DW (1990) Phys Rev B 42:9458
8. Capaldi FM, Boyce MC, Rutledge GC (2004) Polymer 45:1391
9. Barber AH, Cohen SR, Wagner HD (2003) Appl Phys Lett 82:4140
10. Barber AH, Cohen SR, Eitan A, Schadler LS, Wagner HD (2006) Adv Mater 18:83
11. Nishikawa M, Okabe T, Takeda N (2008) Mater Sci Eng A 480:549
12. Nishikawa M, Okabe T, Hemmi K, Takeda N (2008) Int J Solids Struct 45:4098