

Adhesion and reinforcement in carbon nanotube polymer composite

Chenyu Wei^{a)}

NASA Ames Research Center, MS 229-1, Moffett Field, California 94035

(Received 26 September 2005; accepted 19 January 2006; published online 28 February 2006)

Temperature dependent adhesion behavior and reinforcement in carbon nanotube (CNT)-polymer (polyethylene) composite is studied through molecular dynamics simulations. The interfacial shear stress through van der Waals interactions is found to increase linearly with applied tensile strains along the nanotube axis direction, until the noncovalent bonds between CNTs and molecules break successively. A lower bound value about 46 MPa is found for the shear strength at low temperatures. Direct stress-strain calculations show significant reinforcements in the composite in a wide temperature range, with $\sim 200\%$ increase in the Young's modulus when adding 6.5% volume ratio of short CNTs, and comparisons with the Halpin-Tsai formula are discussed.

[DOI: 10.1063/1.2181188]

Since their discovery in the 1990s, carbon nanotubes (CNTs) have been shown to have exceptional mechanical and unique electronic and thermal properties.¹ The large surface area and the high modulus and strength of CNTs¹ make them a good candidate as reinforcing fibers. Recent experiments have shown remarkable enhancements in elastic modulus and strength of polymer composites with an addition of small amounts of CNTs.²⁻⁵ Polymer CNT composites have also been investigated as multifunctional materials for electric and thermal applications.⁶⁻⁸ The adhesion behavior and reinforcement properties are crucial to determine the efficiency of CNTs as nanofibers and the structural stabilities in these CNT composites. While adhesion in CNT composites can be through covalent bonds with specific polymers, noncovalent van der Waals (VDW) interactions are universally present, which have been shown to play an important role for molecule structures at interface and reinforcement in CNT composite,⁹ and is the focus of this study. In this letter we investigate the adhesion behaviors such as interfacial shear stress and bond breaking at large strains, reinforcements in elastic modulus, and their temperature dependence in a polymeric CNT composite, through molecular dynamics simulation method.¹⁰

Polyethylene (PE) is chosen as a model matrix, which is described through a united atom model with bond stretching, bending, and dihedral potentials. A truncated 6-12 Lennard-Jones (LJ)-type VDW interaction is included between CNTs and matrix and within matrix. The details of the force field can be found elsewhere.¹¹ Amber force field¹² is used for the carbon-carbon interactions on CNTs, and the use of which is justified as the embedded CNTs are expected to behave in elastic regime (to be discussed later), due to the weak VDW interactions. The Young's modulus for intrinsic CNTs with Amber force field is found within 10% difference from that with the widely used Tersoff-Brenner potential.¹³

The composite system consists of 50 PE molecules with 100 repeating units and a capped 190-Å-long CNT (10, 0) representing discontinuous fibers, in a periodic unit cell $\sim 26 \times 26 \times 200 \text{ \AA}^3$ (see inset of Fig. 1 for illustration). The system is prepared at 600 K with individual molecules relaxed with Monte Carlo simulation beforehand, and gradually cooled down to low temperatures with a rate of

10 K/100 ps (Berendsen *NPT* ensemble, $P=1$ bar). The details of sample preparation can be found elsewhere.¹¹ Time step of 0.5 fs is used. All the data reported here are averaged over eight sample sets.

To investigate the interfacial adhesion and reinforcement behavior, a tensile stress along the nanotube axis direction is applied to the composite gradually with a rate of 1 bar/1 ps and at each stress there is a responding strain (Berendsen *NPT* ensemble). In this study we focus on the properties induced by the embedded CNTs and the stress/strain rate effect is not discussed. Shown in Fig. 1 is the change in the total interfacial VDW energy, U_{vdw} , between the CNT and the polymer as a function of strain at various temperatures.¹⁴ In comparison, the change in the total VDW energy is also shown for a similarly prepared pure polymer bulk (50 PE with 100 units) at $T=50$ K. It can be seen that the VDW interaction in the composite is much enhanced due to the presence of the nanotube. We attribute such enhancement to two following factors. (1) The large surface area and the high atomic density on the CNT: while the space (6.5% volume ratio) occupied by the CNT would only accommodate 347 matrix (carbon) atoms, there are as many as 1804 atoms on the CNT and all of them are on the surface. (2) The existence of adsorption layer around the CNT, which has a higher density compared with in bulk polymer.⁹ At high temperatures the molecule density in the adsorption layer decreases due to

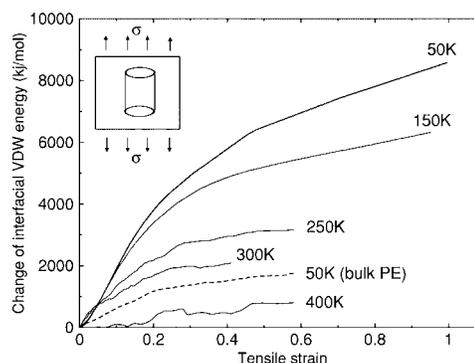


FIG. 1. The change in the total interfacial VDW energy in the PE composite as a function of applied tensile strain at various temperatures from 50 to 400 K (solid lines), in comparison with the change in the total VDW energy in bulk PE at $T=50$ K (dashed line). Inset: Schematic illustration of the unit cell for the composite in simulation, with tensile stress applied along the CNT axis direction.

^{a)}Electronic mail: cwei@mail.arc.nasa.gov

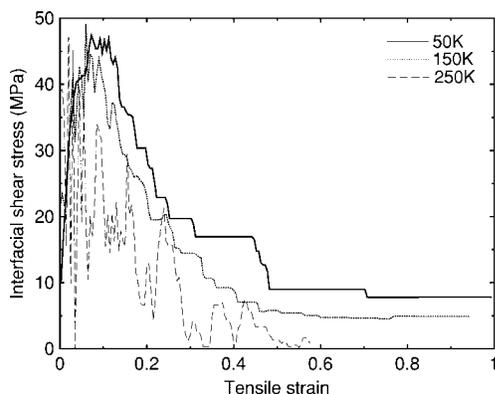


FIG. 2. The interfacial shear stress σ_s in the composite as a function of tensile strain. Solid, dotted, and dashed lines are for $T=50$, 150, and 250 K, respectively. The value of σ_s would extrapolate to zero at $\epsilon=0$.

thermal expansions, which induces a lowered U_{vdw} as shown in Fig. 1.

A frictional force can be defined as $f = -\partial U_{\text{vdw}} / \partial z$, where z is along the CNT axis. The corresponding interfacial adhesion or shear stress can be expressed as $\sigma_s = -A \times f$, where A is the lateral surface area of the CNT. Considering that $\delta z = \ell_0 \delta \epsilon$, where $\ell_0 = \ell_{\text{cnt}}$ is the length along CNT lateral surface and ϵ is the strain in the composite along z direction, σ_s can be further expressed as follows:

$$\sigma_s = \frac{1}{2\pi r_{\text{cnt}} \ell_{\text{cnt}}} \frac{1}{\ell_{\text{cnt}}} \frac{\partial U_{\text{vdw}}}{\partial \epsilon}, \quad (1)$$

where r_{cnt} is the radius of the CNT. Taking $r_{\text{cnt}} \sim 3.9 \text{ \AA}$ and $\ell_{\text{cnt}} \sim 185 \text{ \AA}$ (excluding the caps¹⁵) into Eq. (1), the calculated σ_s is shown in Fig. 2 as a function of strain at various temperatures ($\partial U_{\text{vdw}} / \partial \epsilon$ is calculated as $\Delta U_{\text{vdw}} / \Delta \epsilon$ with $\Delta \epsilon = 0.005$). First we discuss the low temperature $T=50 \text{ K}$ case. From Fig. 2 it can be seen that σ_s increases linearly with the strain as $\sigma_s = 967 \text{ MPa} \times \epsilon$ (for $\epsilon < 5\%$). This linear behavior is expected as the interfacial energy can be modeled as a harmonic potential in the elastic regime. The shear stress reaches its maximum strength $\tau \sim 46 \text{ MPa}$ around $\epsilon \sim 10\%$. Beyond that σ_s is no longer strong enough to hold the interfacial bonds. The breaking of the bonds is confirmed by the decrease in σ_s at large ϵ . An interesting feature is that σ_s decreases in a staircase manner, suggesting that the bond breaking is not simultaneous. An averaged shear strength per site on the CNT is estimated as $\sim 0.025 \text{ MPa}$, which is less than the smallest loss of σ_s (1.0 MPa at $T=50 \text{ K}$, 0.3 MPa at $T=150 \text{ K}$) between any two adjacent staircases shown in Fig. 2, indicating that the bonds can break in group at multiple sites. These bond breaking behaviors are more complicated compared within the stick-slip model for microfriction between crystallized solid surfaces,¹⁶ due to the long length and amorphous nature of the polymer molecules. The overall value of the shear stress decreases with the increase of temperature, as shown in Fig. 2, due to the similar reason mentioned above for the decrease of U_{vdw} at high temperatures. The increased thermal fluctuations also would destabilize the interfacial bonding. At $T=250 \text{ K}$ the occasional increase in σ_s at high strains indicates bond reformations, which is not observed at low temperatures, as the fast stress rate in the simulation does not encourage bond reformations in a short time scale, which is much fastened at high temperatures.

The calculated shear strength $\sim 46 \text{ MPa}$ provides a lower bound for τ , as only VDW interactions are included,

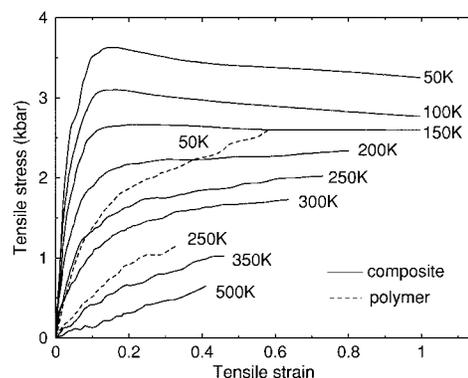


FIG. 3. The applied tensile stress vs the responding strain for the PE-CNT composite at various temperatures from 50 to 500 K (solid lines), in comparison with that for bulk PE at $T=50$ and 250 K (dashed lines).

which is in excellent agreement with experiment measured $\tau \sim 47 \text{ MPa}$ between polyethylene-butene matrix and multi-walled CNTs.¹⁷ For large radius CNTs other than the CNT (10, 0) in this study, τ can be slightly lower due to the curve effect on adsorption energies. The value of τ could increase when strong covalent bonds^{18,19} or extra contributions from electrostatic interactions exist.²⁰ Previous pullout simulations of CNTs from polystyrene (PS) matrix showed $\tau \sim 150 \text{ MPa}$, including both VDW and electrostatic interactions, although separated contributions were not discussed there.²⁰ Differences in the atomic compositions of PE and PS molecules could also contribute to the difference in τ , as previous simulation studies have suggested that presences of large base or side groups in polymer molecules can lead to a stronger VDW interaction with CNTs.²¹

The reinforcement of the composite is investigated from direct stress-strain calculations. The applied stress as a function of the responding strain is plotted in Fig. 3 at various temperatures. The composite behaves as a glass solid at low temperatures ($T < 300 \text{ K}$), and its mechanical response is much weakened at high temperature. In comparison the stress-strain curve for the pure polymer bulk is also shown for $T=50$ and 250 K. It can be seen clearly that there are strong reinforcements in the composite in both the small and large strain regimes. This is mainly due to the much enhanced VDW interfacial interactions described above, while the contributions from the bond stretching, bending and torsion of the molecules are much smaller. The radical distribution function of bond length shows that the strain induced on the CNT is within 1%, justifying the use of Amber force field in this case. Both the composite and the bulk polymer yield around $\epsilon \sim 10\%$ at low temperatures, after which the stress-strain curve is away from the linear regime. The continuing increase of stress in the polymer bulk beyond yielding can be attributed to the entanglement of the polymer chains for the mechanical responses. Such entanglement is expected to be much less in the composite as the molecules prefer alignment along the nanotube, which can result in enhanced brittleness as observed in CNT composites.² At low temperatures (50, 100, and 150 K) the composite is found to break in the matrix region at the maximum strain, while no breaking is observed in other cases (including polymer bulk at $T=50$ and 250 K) up to the maximum strain.¹⁴

The Young's modulus Y of the composite is calculated from the stress-strain curve within $\epsilon < 5\%$, and plotted in Fig. 4 as a function of temperature, in comparison with that

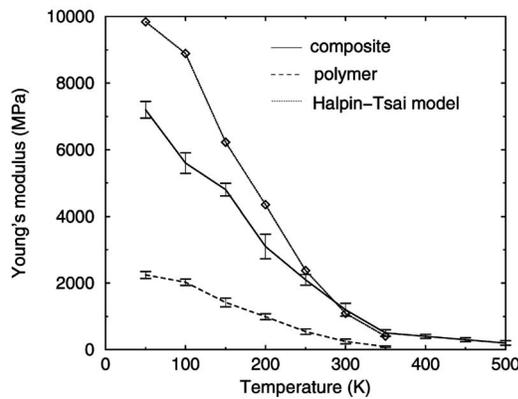


FIG. 4. Young's modulus of the PE-CNT composite (solid line) as a function of temperature, in comparison with that of the bulk PE (dashed line), and also in comparison with the value from the Halpin-Tsai formula (diamond and dotted line). The error bars for data from MD simulation are also shown.

of the bulk polymer. A large increase in Y is observed over a wide temperature range with $T < 350$ K. At $T = 50$ K, Y is as high as 7200 MPa for the composites, which is 220% increase than the 2245 MPa for the polymer bulk. Similar increases are also found at other temperatures. The Young's modulus for both systems decreases dramatically above 350 K to near zero values at high T . This is expected as the systems are in viscous or liquid state above the glass transition temperature (~ 300 K from density-temperature function).

The degree of reinforcement of a composite depends on the aspect ratio and alignment of fibers. The Halpin-Tsai formula, based on force balance model and empirical data, is used widely for macroscopic composites.²² According to such formula the Young's modulus of a composite with aligned and discontinuous fibers can be expressed as follows:

$$Y_{\text{comp}} = Y_m(1 + \xi\eta V_f)/(1 - \eta V_f), \quad (2)$$

with $\eta = (Y_f/Y_m - 1)/(Y_f/Y_m + \xi)$ and $\xi = 2(L/D)$. Y_f and Y_m are the Young's modulus for the fiber and matrix, respectively; V_f and L/D are the volume ratio and aspect ratio of the fiber, respectively. From Eq. (2) it can be seen that Y_{comp} strongly depends on the geometry of the fibers such as their aspect ratio. For continuous fibers with $\xi \rightarrow \infty$, Eq. (2) reduces to the rule of mixture $Y_{\text{comp}} = Y_m V_m + Y_f V_f$, which provides an upper limit for reinforcements in a fiber composite. Taking $V_f \sim 6.5\%$, $L/D \sim 24$, and $\eta \sim 1$ (as $Y_f \sim 1$ Tpa $\gg Y_m$), the predicted value of Y based on Eq. (2) is shown in Fig. 4. It can be seen that at low temperatures the Halpin-Tsai formula gives a higher value for Y (36% higher at $T = 50$ K) compared with that from the molecular dynamics simulation. Such difference can come from the fact that the Halpin-Tsai model is based on continuum elastic medium approximation and does not take into account the molecule structures at interfaces, which have been shown to be very different from bulk in densities and orientations.⁹ A load transfer model based on substrate interaction and molecule wrapping geometry suggested that less perfect coverage of molecules on CNTs can lead to a smaller Young's modulus than that from the Halpin-Tsai formula.²³ Recent experiments on poly(vinyl alcohol)³ and polypropylene CNT composites²⁴ have also shown disagreements in measured modulus or CNT lengths with predicted values based on the Halpin-Tsai model. The

difference in the value of Y diminishes at high temperature ($T > 250$ K) as shown in Fig. 4. It could be due to the increased thermal fluctuations making the interfacial structures at atomic level less important and thus the continuum medium approximation in the Halpin-Tsai formula becomes appropriate. Future studies are needed on this subject.

In summary, we have studied the adhesion behavior and reinforcement in a model PE-CNT composite. The interfacial shear stress is found to increase linearly with the applied strain in small strain regime and a lower bound value for the shear strength is found ~ 46 MPa at low temperatures. Such value decreases with the increase of temperature. At large strains the interfacial bonds break successively with the shear stress decreasing in a staircase manner. The mechanical properties of the composite are found to be largely enhanced over a wide temperature range from 50 to 350 K compared with the bulk polymer, due to the enhanced VDW interactions. The degree of increase in the Young's modulus is around 200% for the composite in this study, and the difference with that from the continuum medium approximation based Halpin-Tsai formula suggests that interfacial atomic structure is crucial for a nanocomposite.

This work is partially supported by NASA Contract No. NAS2-03144 to UARC.

¹For detailed review, see P. J. K. Harris, *Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century* (Cambridge University Press, Cambridge, UK, 1999).

²K. Lozano and E. V. Barrera, *J. Appl. Polym. Sci.* **79**, 125 (2000).

³M. Cadek, J. N. Coleman, K. P. Ryan, V. Nicolos, G. Bister, A. Fonseca, J. B. Nagy, K. Szostak, F. Beguin, and W. Blau, *Nano Lett.* **4**, 353 (2004).

⁴R. Sen, B. Zhao, D. Perea, M. E. Iktis, H. Hu, J. Love, E. Bekyarova, and R. C. Haddon, *Nano Lett.* **4**, 459 (2004).

⁵X. Li, H. Gao, W. A. Scrivens, D. Fei, X. Xu, M. A. Sutton, A. P. Reynolds, and M. L. Myrick, *Nanotechnology* **15**, 1416 (2004).

⁶J. M. Benoit, B. Corraze, and O. Chauvet, *Phys. Rev. B* **65**, 241405 (2002).

⁷B. E. Kilbride, J. N. Coleman, J. Frayssé, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth, and W. J. Blau, *J. Appl. Phys.* **92**, 4024 (2002).

⁸M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, A. T. Johnson, and J. E. Fischer, *Appl. Phys. Lett.* **80**, 2767 (2002).

⁹C. Wei, K. Cho, and D. Srivastava, *Nano Lett.* **4**, 1949 (2004).

¹⁰DLPOLY code is obtained from Daresbury Laboratory, UK.

¹¹C. Wei, D. Srivastava, and K. Cho, *Nano Lett.* **2**, 647 (2002).

¹²W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, and P. Kollman, *J. Am. Chem. Soc.* **117**, 5179 (1994).

¹³J. Tersoff, *Phys. Rev. B* **37**, 6991 (1988); D. W. Brenner, *ibid.* **42**, 9458 (1990).

¹⁴Extensions beyond the maximum strains shown in Fig. 1 are not available as the simulation requirement of half of the unit cell size not smaller than the cutoff distance of LJ potential is reached, due to the contraction in the transverse plane.

¹⁵Effects from the two caps are omitted as there is only a fraction of atoms (60 out of 1804) on them.

¹⁶G. A. Tomlinson, *Philos. Mag.* **7**, 905 (1929).

¹⁷A. H. Barber, S. R. Cohen, and H. D. Wagner, *Appl. Phys. Lett.* **82**, 4140 (2003).

¹⁸H. D. Wagner, O. Lourie, Y. Feldman, and R. Tenne, *Appl. Phys. Lett.* **72**, 188 (1998).

¹⁹S. J. V. Frankland, A. Caglar, D. W. Brenner, and M. Griebel, *J. Phys. Chem. B* **106**, 3046 (2002).

²⁰K. Liao and S. Li, *Appl. Phys. Lett.* **79**, 4225 (2001).

²¹M. Yang, V. Koutsos, and M. Zaiser, *J. Phys. Chem. B* **109**, 10009 (2005).

²²J. C. Halpin and J. L. Kardos, *Polym. Eng. Sci.* **16**, 344 (1976).

²³A. Wall, J. N. Coleman, and M. S. Ferreira, *Phys. Rev. B* **71**, 125421 (2005).

²⁴T. E. Chang, L. R. Jensen, A. Kisliuk, R. B. Pipes, R. Pyrz, and A. P. Sokolov, *Polymer* **46**, 439 (2005).