Reinforcement Mechanisms in Polymer Nanotube Composites: Simulated Non−Bonded and Cross−Linked Systems

S. J. V. Frankland[1], A. Caglar[2], D. W. Brenner[1], M. Griebel[2]
[1]Department of Materials Science and Engineering, North Carolina State University, Raleigh,NC
[2]Department of Applied Mathematics, Division of Scientific Computing and Numerical Simulation, University of Bonn, Germany.

ABSTRACT

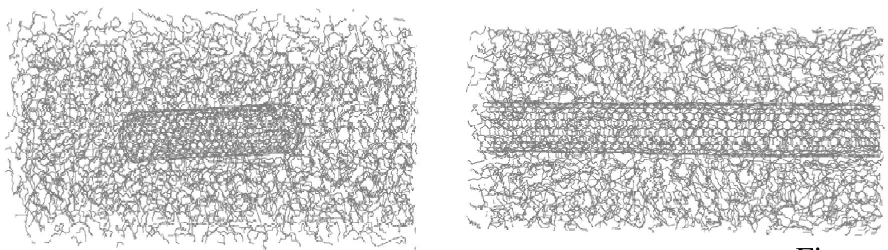
A summary of three simulations related to the issue of load transfer in carbon nanotube/polymer composites is given. Each simulation considers a (10,10) nanotube in a polyethylene matrix modeled with either a united−atom or fully−atomic polyethylene representation. The first simulation uses molecular dynamics to model a 100 nm nanotube in polyethylene in which the nanotube and matrix interact through weak non−bonded interactions. No permanent stress transfer is observed for this system. The second simulation estimates the shear yield strength for the nanotube in each of the model polyethylene matrices. The third simulation addresses a chemically functionalized nanotube in which there are cross−links between the nanotube and matrix. The results indicate that the cross−linked system has an enhanced shear yield strength of one to two orders of magnitude larger than the non−bonded composites.

INTRODUCTION

Composite materials consisting of carbon nanotubes in polymer matrices are potential future lightweight high−strength fiber−reinforced materials [1]. For carbon nanotubes to act as reinforcing fibers significant load transfer must exist between the polymer and the nanotube. Mechanisms and magnitudes of load transfer between polymer matrices and nanotubes remain in question. Enhanced moduli in various polymer matrices indicate that nanotubes may carry some of the load [2–3 4 5 6]. Fragmentation studies [7,8] suggest that there is some stress transfer in composites, but Raman evidence [2,9] shows that slippage between the shells of multi−wall nanotubes and within single−wall nanotube ropes may limit stress transfer. One possible way to strengthen the interface between nanotubes and polymer matrices is with chemical bonding. Such functionalization may be responsible for the stress transfer amount of 500 MPa estimated in epoxy/nanotube composites []. Complexation with polymethylmethacrylate [10,11] has been reported, as has direct functionalization of nanotube sidewalls [12–13 14], but it is possible that functionalizing nanotubes in composites may weaken properties such as tensile strengths and reduce the strain before yield due to the introduction of sp^3 hybridized sites. However, according to a computational estimate on ethyne functionalized nanotubes, the maximum buckling force in compression may only be reduced by about 15 % [15].

The simulations discussed here were carried out to investigate the conditions under which stress transfer may occur in composite materials, and therefore provide insight on how to optimize these composites. The simulations, though still somewhat preliminary, build on earlier work with (10,10) nanotubes in polyethylene (PE) matrices[16]. Polyethylene was chosen, not because it would be the polymer of choice to make such composites from, but because it is a convenient model system for simulation. It has a simple monomer that is conducive to forming a chain of polymer beads. Also, as a fully hydrocarbon system, it can be represented with a many−body bond order potential which further allows creation of rehybridized chemical bonds to the nanotube. Three simulations are presented. In the first study, a molecular dynamics simulation was carried out in which a composite is strained and the resulting stress analyzed. In the second set of simulations, a critical shear yield strength was calculated using a simulated "pull–through" experiment. The shear yield strength was in turn used to estimate how long the load bearing length of the nanotube should be according to the potentials used in the first simulation. The third simulation considers the effect of cross–linking the nanotube to the polymer matrix on the critical nanotube–matrix shear yield strength.

COMPUTATIONAL METHODS



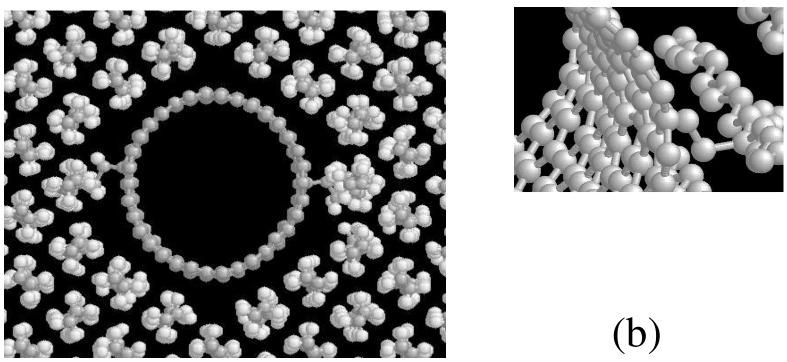
(a) (b)

Figure 1: (a) Configuration in MD and EM simulations and (b) in shear yield strength estimates.

Figure 1a illustrates the configuration of the sample composite modeled in the first set of simulations. A PE matrix surrounds a capped 100 nm long (10,10) single–walled nanotube. The system was periodic in three directions with box dimensions ~5x5x200nm. The PE was represented by chains of united CH_2 "atoms" and contained a total of ~181000 atoms. The PE potential function is described in more detail elsewhere []. The molecular dynamics simulations were carried out using DL–POLY[17], a large–scale molecular dynamics simulation package available from Daresbury Laboratory. This package was adapted to include a many–body bond order potential for the carbon nanotube [18]. The simulations were run with a timestep of 2 fs at a temperature of 300 K. After equilibrating the system, strain was applied to the system in 2% increments per 2500 steps by rescaling the atomic positions and box size in the direction parallel to the nanotube axis. The resulting atomic level hydrostatic stresses [19] in the system were analyzed.

In the second set of simulations, two PE representations were compared, one with the united–atom potential described above, and a second one which explicitly included hydrogen atoms. The fully–atomic PE sample was equilibrated via an energy minimization method developed by Caglar and Griebel that employs a conjugate–gradient method for relaxing the system to its local energy minimum. The potential used was the hydrocarbon form of the many–body bond order function used for the nanotube [18,20]. The sample configuration for estimating the shear yield strength of the nanotube in the polyethylene matrix is illustrated in Figure 1b. In these simulations a uniform one–body force was added to the atoms that comprise the nanotube, and the magnitude of this force at which the nanotube began to move freely independent of the matrix was recorded. The matrix was held rigid while the nanotube was free to move at 300K and a timestep of 2fs. The shear yield strength was estimated as the total applied force divided by the surface area of the nanotube. In other words, the quantity measured was the stress required for the nanotube to break free of the matrix. The simulation box dimensions were ~5x5x10 nm where the longest dimension is parallel to the nanotube axis.

In the third set of simulations, the shear yield strength of a nanotube chemically bonded to a crystalline matrix was estimated in a similar manner to that outlined above. The system used periodic boundaries with a box size of 5x5x2.5nm where the shortest dimension is parallel to the nanotube axis. Two cross–links between the 400–atom nanotube and the surrounding matrix were created by replacing one hydrogen atom per cross–link on a chain surrounding the nanotube with a short, 2 monomer unit section of a polyethylene chain. The other end of the cross–link was held near one of the carbon atoms in the nanotube, and allowed to interact and form a bond in which the nanotube carbon atom effectively rehybridized from sp^2 to sp^3. Hydrogen atoms were included in the PE chains yielding a fully–atomic representation. This simulation, which was carried out with software developed by Brenner et al. [18] used a mobile, rather than rigid, crystalline PE matrix at 300K and a timestep of 0.2 fs.



(a) (b)

Figure 2: Illustration of the crystalline PE matrix with a nanotube chemically bonded to nearby chains. (a) View down the nanotube axis. (b) View showing the cross–link.

RESULTS AND DISCUSSION

Plotted in Figure 3 are atomic level stresses along the 100 nm nanotube averaged per atom from the first set of simulations as a function of position along the nanotube. The results are representative of all of the 2% increments that were simulated. At the instant when strain was initially applied at 2%, the nanotube, together with the rest of the composite, was under

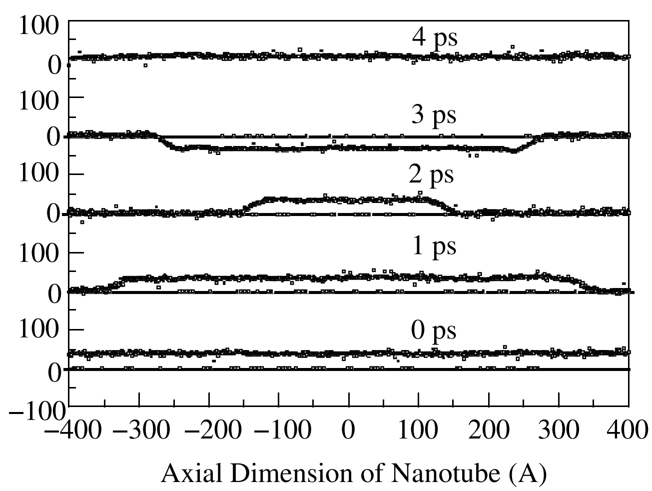


Figure 3: Hydrostatic stress along the 100 nm nanotube averaged per atom from the first set of simulations. The curves begin at 0 ps when the strain is initially applied to 4 ps where the stress is completely dissipated.

tensile stress (positive value in Figure 3). As the simulation progresses, stress in the nanotube was not released uniformly, but was released first at the ends of the nanotube. The initial tension was largely released by about 2 ps. After 3 ps, the nanotube was under compressive stress (negative value in Figure 3). By 4 ps, it relaxed. The nanotube showed no permanent stress transfer from the matrix, but rather behaved like a rubber band 'ringing'. This result agrees with previous simulations [] that also showed no permanent stress transfer for a very short nanotube of 6 nm in length. Here the nanotube is somewhat longer, but the result is the same.

Shear yield strengths obtained from the second set of simulations confirm the MD results. The shear yield strength of the nanotube in the amorphous united–atom composite is estimated to be ~0.7 MPa. An estimate for the critical length l_c for maximum load transfer can be obtained from the equation

$$l_c = \sigma_f d / 2\tau_c \qquad (1)$$

where σ_f is the fiber tensile strength, d is the fiber diameter, and τ_c is the fiber–matrix shear yield strength. Assuming a σ_f of 50 GPa (a reasonable value based on recent experiments [21,22]), the minimum load bearing length of this nanotube should be about 100 microns. Improving the potential representation to explicitly include hydrogen atoms produces a composite with a higher yield strength of ~5 MPa, and therefore a critical length about an order of magnitude shorter at 10 microns critical length. Both of these estimates result from the weak non–bonded forces between the matrix and the nanotube. They are not only too long to simulate, but also too long to be practical for fiber reinforced composites using nanotubes.

A functionalized composite in which nanotubes are chemically bonded to the polymer matrix should represent a much stronger nanotube–matrix interaction. With the addition of the two cross–links illustrated in Figure 2, the shear yield strength was estimated to increase to about 70 MPa, an increase over the non–bonded systems of one to two orders of magnitude. How much of the improvement comes from the crystalline nature of the PE rather than the bonds is not as yet clear, but this result is potentially very promising as it reduces the critical length to order of 1 micron, a reasonable length for the production of single–walled nanotubes.

CONCLUSIONS

Results from three simulations designed to examine load transfer in polymer–nanotube composite materials were presented. For strictly non–bonded nanotube–matrix interactions, the simulations predict that nanotubes with lengths in excess of 10–100 microns are needed for significant load–bearing ability. In contrast, the simulations predict a one to two order of magnitude increase in shear yield strength for a nanotube cross–linked to the polymer matrix relative to systems without cross–links. The critical length for the cross–linked system is, therefore, reduced to ~1 micron.

ACKNOWLEDGMENTS

The authors thank S. B. Sinnott for providing structures for the nanotube caps, and O. A. Shenderova and S. P. Adiga for helpful discussions. The work was supported by a Multi–University Research Initiative of the Office of Naval Research through the North Carolina Center for Nanoscale Materials and the NASA–Ames Computational Nanotechnology Program. It was further supported by the SFB 256 of the University of Bonn. The simulations were carried out on facilities at the North Carolina Supercomputing Center and on Parnass2 at the Department of Applied Mathematics, University of Bonn.

REFERENCES

[1] . P. Calvert, *Nature* **399**, 210 (1999).
[2] . L. S. Schadler, S. C. Giannaris, and P. M. Ajayan, *Appl. Phys. Lett.* **73**, 3842 (1998).
[3] . X. Gong, J. Liu, S. Baskaran, R. D. Voise, and J. S. Young, *Chem. Mater*. **12**, 1049 (2000).
[4] . R. Haggenmueller, H. H. Gommans, A. G. Rinzler, J. E. Fischer, and K. I. Winey, *Chem. Phys. Lett.* **330**, 219 (2000).
[5] . D. Qian, E. C. Dickey, R. Andrews, and T. Rantell, *Appl. Phys. Lett.* **76**, 2868 (2000).
[6] . M. S. P. Shaffer and A. H. Windle, *Adv. Materials* **11**, 937 (1999).
[7] . H. D. Wagner, O. Lourie, Y. Feldman, and R. Tenne, *Appl. Phys. Lett*. **72**, 188 (1998).
[8] . O. Lourie and H. D. Wagner, *Appl. Phys. Lett*. **73**, 3527 (1998).
[9] . P. M. Ajayan, L. S. Schadler, C. Giannaris, and A. Rubio *Adv. Materials* **12**, 750 (2000).
[10]. M. Lamy de la Chapelle, C. Stephan, T. P. Nguyen, S. Lefrant, C. Journet, P. Bernier, E. Munoz, A. Benito, W. K. Maser, M. T. Martinez, G. D. de la Fuente, T. Guillard, G. Flamant, L. Alvarez, and D. Laplaze, *Synthetic Metals* **103**, 2510 (1999).
[11]. Z. Jia, Z. Wang, C. Xu, J. Liang, B. Wei, D. Wu, and S. Zhu, *Mat. Sci. Eng. A* **271**, 395 (1999).
[12]. J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, and R. C. Haddon, *Science* **282**, 95 (1998).
[13]. E. T. Michelson, I. W. Chiang, J. L. Zimmerman, P. J. Boul, J. Lozano, J. Liu, R. E. Smalley, R. H. Hauge, and J. L. Margrave, *J. Phys. Chem. B* **103**, 4318 (1999).
[14]. P. J. Boul, J. Liu, E. T. Michelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave, and R. E. Smalley, *Chem. Phys. Lett*. **310**, 367 (1999).
[15]. A.Garg and S. B. Sinnott, *Chem. Phys. Lett*. **295**, 273 (1998)
[16]. S. J. V. Frankland and D. W. Brenner in *Amorphous and Nanostructured Carbon,* edited by J. P. Sullivan, J. Robertson, O. Zhou, T. B. Allen, and B. F. Coll (Mat. Res. Soc. Symp. Proc., **593,** Warrendale, PA, 1999) pp. 199.
[17]. T. R. Forester and W. Smith, *The DL_POLY User Manual Version 2.11*, CCLRC, Daresbury Laboratory, Daresbury, 1998.
[18]. D. W. Brenner, *Phys. Rev. B* **42**, 9458 (1990). A slightly modified form is used for the present calculations. (D. W. Brenner, O. A. Shenderova, S. B. Sinnott, and J. A. Harrison, unpublished).
[19]. V. Vitek and T. Egami, Physica Status Solidi B **144**, 145 (1987).

[20]. A. Caglar and M. Griebel in *Molecular Dynamics on Parallel Computers*, World Scientific, Singapore, 2000.
[21]. M. F. Yu, B. S. Files, S. Arepalli, and R. S. Ruoff, *Phys.Rev. Lett*. **84**, 5552 (2000).
[22]. M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, *Science* **287**, 637 (2000).