Molecular Simulation of the Influence of Chemical Cross-Links on the Shear Strength of Carbon Nanotube−Polymer Interfaces

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Received: November 27, 2001; In Final Form: February 13, 2002

The influence of chemical cross-links between a single-walled fullerene nanotube and a polymer matrix on the matrix−nanotube shear strength has been studied using molecular dynamics simulations. A (10,10) nanotube embedded in either a crystalline or amorphous polyethylene matrix is used as a model for a nonbonded interface (in the absence of cross-links). The simulations predict that shear strengths and critical lengths required for load transfer can be enhanced and decreased, respectively, by over an order of magnitude with the formation of cross-links involving less than 1% of the nanotube carbon atoms. At this level of chemical functionalization, calculations also predict that there is a negligible change in tensile modulus for a (10,10) nanotube.

I. Introduction

Composites of carbon nanotubes in polymer matrices have potential as lightweight high-strength fiber-reinforced materials.[1] For carbon nanotubes to act as reinforcing fibers, significant load transfer must exist between the polymer matrix and the nanotube. To date, both the mechanisms and magnitudes of load transfer between polymer matrices and nanotubes remain unclear. Enhanced moduli in various polymer matrices indicate that nanotubes may carry some of the load.[2−6] 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 multiwall nanotubes and within single-wall nanotube ropes may limit stress transfer.

Molecular mechanics simulations predict maximum frictional stresses from 18 to 135 MPa for sliding (10,10) nanotubes within single polymer chains.[10] For the polymers modeled, little correlation was found between interfacial energy and maximum shear stress. It was suggested that helical polymer conformations in which chains can wrap around nanotubes may enhance nonbonded nanotube−polymer interactions.

Another possible way to strengthen the interface between nanotubes and polymer matrices is with chemical bonds. Chemical bonding, for example, has been suggested as responsible for the stress transfer value of 500 MPa estimated in epoxy/nanotube composites.[7] Complexation with poly(methyl methacrylate)[11,12] has been reported, as has direct functionalization of nanotube sidewalls,[13−15] but it is possible that functionalizing nanotubes in composites may compromise properties such as tensile modulus and strength due to the introduction of sp^3 hybridized sites. For example, according to a computational estimate on ethyne functionalized nanotubes the maximum force prior to buckling in compression can be reduced by 15% due to functionalization.[16]

Here an estimate is made for changes in fiber−matrix shear strengths in a composite with weak nonbonded polymer−nanotube interactions and in a similar composite with a low density of chemical cross-links at the polymer−nanotube interface.[17] The parameter used to gauge the effect is the minimum shear stress τ_c that must be applied to the nanotube to pull it through the polymer matrix. The critical length l_c of a nanotube required for strong load transfer can be estimated from τ_c by the expression

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

where σ_f is the fiber tensile strength and d is the fiber diameter for a solid fiber.[18] Reported below are values for τ_c and the corresponding l_c from eq 1 for both nonbonded and chemically cross-linked interfaces between a (10,10) nanotube and either a crystalline or amorphous polyethylene matrix. This system was chosen to study the effects of cross-links because of its simplicity, and not because it is necessarily experimentally accessible, or because it would make a composite with particularly strong interfacial interactions. It is a convenient system for which the polymer, nanotube, and any chemical bonding between them can be consistently modeled with a hydrocarbon potential. Crystalline and amorphous structures are representative elements of polymers, and their examination gives a general picture of the possible behaviors of polymer−nanotube composites.

II. Computational Methods

The model systems were composed of a single-walled (10,10) nanotube embedded into either a crystalline or amorphous matrix. Periodic boundaries were used, and in each case studied the nanotube spanned the total length of the periodic cell in one direction, resulting in a nanotube−matrix system of infinite length. A many-body bond-order potential was used to describe the intramolecular interactions in the nanotube, polymer chains, and cross-links.[19] The potential function allows the formation of chemical bonds, with appropriate atomic rehybridization,

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10.1021/jp015591+ CCC: $22.00

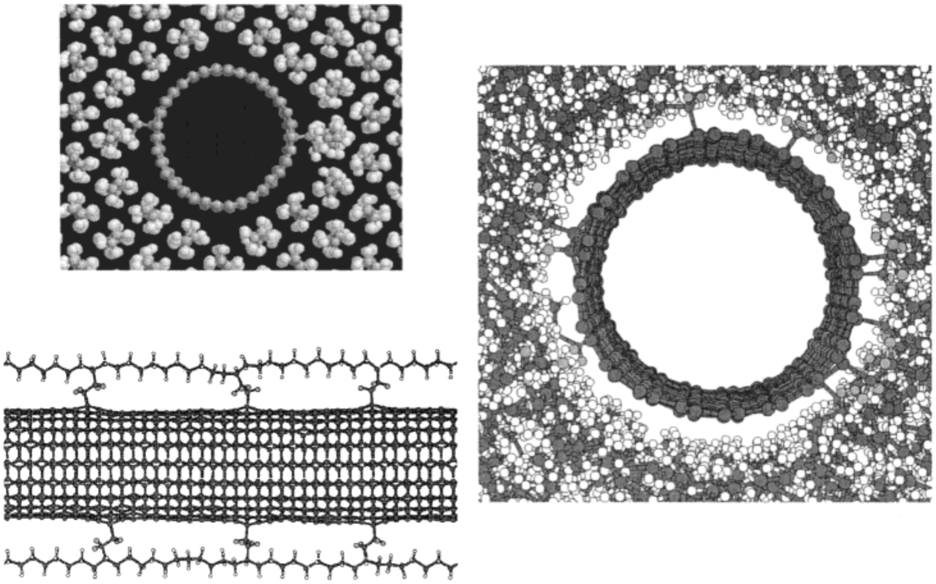

Figure 1. Illustration of the cross-linked systems. Left: crystalline matrix. Right: amorphous matrix.

between the nanotube and polyethylene. All nonbonded interactions within the polyethylene matrix and between the matrix and nanotubes were modeled with Lennard-Jones 6-12 potentials with parameters taken from reference 20.

The matrix for the crystalline system was initially generated from the experimental crystal structure of polyethylene with the polymer chains parallel to the nanotube axis. An appropriate number of polymer chains at the center of the matrix were then replaced with a (10,10) nanotube of length 53 Å This size was chosen because it accommodates the translational repeat units of the matrix and nanotube. This system contained 880 carbon atoms in the nanotube, and 178 chains of 42 methylene units in the matrix. Both the nanotube and polymer chains were replicated across the periodic boundaries of the simulation cell. The initial system was equilibrated to 300K via molecular dynamics simulation (MD) using the interatomic forces described above. After equilibration, a total of 6 cross-link chains containing 2 methylene units each were created between the nanotube and matrix. The resulting system is illustrated in Figure 1. This kind of functionalization may remove an unpaired electron from the nanotube pi system leaving another unpaired electron able to scavange a hydrogen atom or form a separate linkage to the polymer chain. We chose not to include this effect as it is not clear with the molecular modeling technique being used that the unpaired electron would necessarily occur on an adjacent nanotube carbon, and we are primarily interested in how the shear yield strength is affected by adding cross-links between the matrix and the nanotube, rather than fully representing the chemistry of functionalizing the nanotube.

The amorphous matrix contained eight polymer chains, each with 1095 repeat units. To generate the amorphous structure, the chains were initially treated within a united atom approximation, and the chain coordinates were randomly generated on a diamond lattice surrounding the nanotube. The matrix was then equilibrated to 300K via MD assuming constant carbon−carbon bond lengths of 1.53 Å (via the SHAKE algorithm[20]) using appropriate bond bending, bond torsion, and united-atom nonbonded interactions[21] while holding the nanotube rigid. The system was further equilibrated with a nonrigid nanotube, including scaling the box and system coordinates to create a zero initial stress state. Explicit hydrogen atoms were then added to the matrix chains, and the potential energy of the system was minimized via a conjugate-gradient method[22] using the potential described above after which the system was reequilibrated to 300K with MD. The resulting amorphous structure had a density of 0.71 g/cm^3 that is slightly less than the crystalline matrix density 0.94 g/cm^3. A total of 6 cross-links with 2 methylene units each were formed between the nanotube and matrix after equilibration, yielding a grafting density of ~0.3%. A sample configuration is illustrated in Figure 1.

TABLE 1: Calculated Values for τ_c and l_c for Non-Bonded and Cross-Linked Systems

	τ_c (MPa)	l_c (μm)
Non-Bonded Composites		
amorphous	2.7 ± 0.2	30 ± 2
crystalline	2.8 ± 0.3	29 ± 2
Cross-Linked Composites		
amorphous		
initial nanotube motion	2.0 ± 0.3	40 ± 7
chain and nanotube motion	30 ± 3	2.6 ± 0.2
crystalline		
initial nanotube motion	6.8 ± 0.2	11.7 ± 0.3
chain and nanotube motion	110 ± 13	0.72 ± 0.08

To estimate the shear strengths between the nanotubes and matrices, MD simulations were carried out in which a uniform one-body force was added to the atoms that comprise the nanotube. The shear strength τ_c between the nanotube and matrix was taken as the total force at which the center of mass of the nanotube began to move freely independent of the matrix normalized by the nanotube surface area ($r = 8.0$ Å. The resulting data generated by these simulations are given in Table 1. The values for τ_c and respective critical lengths are averaged from three trials and the uncertainties reported are the standard deviations of the three measurements. Equation 1 is used to estimate the critical fiber length l_c for efficient load transfer assuming a σ_f of 50 GPa based on recent experiments.[23]

The MD simulations of the composites were performed with the DL-POLY simulation package modified to include the many body bond-order hydrocarbon potential.[24]

III. Results and Discussion

Both the amorphous and crystalline matrix models produce similar shear yield strengths (Table 1) in the nonbonded composites. Therefore similar critical lengths for load transfer are predicted despite the difference in density and structure between the two matrices. This result suggests that for this system the details of the matrix have a small effect on load transfer, or that the sample size is too small to pick up the effects of long-range order of the matrix. In these simulations no electrostatic interactions are included to supplement the relatively weak Lennard-Jones forces. Therefore, the values of τ_c from these simulations provide an estimate of the lower limit of what can be expected for nonbonded polymer–nanotube composites.

For the cross-linked systems, two processes were observed in pulling the nanotubes through the composites, and therefore two sets of τ_c values are reported. The lower τ_c values correspond to the applied force at which a nanotube alone begins to shear with respect to the matrix. The higher value of τ_c was determined from the initial force at which the nanotube pulls the polyethylene chains with it through the matrix. For the amorphous composite the lower value of τ_c is comparable to the nonbonded systems. In the crystalline composite the nanotube has a higher initial τ_c in these composites by about a factor of 2 over the nonbonded composite. This result indicates that even the initial yielding may be reinforced, albeit by a relatively small amount. In both the amorphous and crystalline matrices the shear strength required to begin pulling the chains through the matrix is about 15 times that needed to initiate the initial motion of the nanotube, resulting in a corresponding shortening of the critical fiber needed for good load transfer.

These results suggest that even a relatively low density of cross-links can have a large influence on the properties of nanotube–polymer interfaces. To estimate whether this degree of functionalization would alter the tensile strength of nanotubes, simulations were carried out in which methyl radicals were chemisorbed to random sites on an isolated (10,10) nanotube of infinite length (via periodic boundaries) at different grafting densities. The systems were then strained in small increments along the nanotube axis and relaxed to their minimum energy configurations at constant strain up to a total strain of 2%. The modulus as a function of grafting density was then determined by assuming that the deformation along the nanotube was harmonic, with a value of the elastic modulus determined from the energy–strain relations. These calculations predict that for a (10,10) nanotube there is a negligible change in modulus for functionalization of at least up to 10% of the carbon atoms in the nanotube.

IV. Conclusions

Using molecular simulations, it has been concluded that the shear strength of a polymer–nanotube interface with weak nonbonded interactions can be increased by over an order of magnitude with the introduction of a relatively low density ($<1\%$) of chemical bonds between the nanotube and matrix. Our model also predicts that the change in tensile modulus of a (10,10) nanotube with this level of functionalization is negligible. These results, taken together, suggest that load transfer and, hence, modulus of nanotube–polymer composites can be effectively increased by deliberately adding chemical cross-linking. It also supports suggestions that inadvertent chemical bonding between nanotubes and polymer matrices during processing may be in part responsible for the enhanced stress transfer observed in some systems of this type.[7]

Acknowledgment. The authors thank S. B. Sinnott, O. A. Shenderova, S. P. Adiga, and J. D. Schall for helpful discussions. S.J.V.F. and D.W.B. were supported by a Multi-University Research Initiative of the Office of Naval Research through the North Carolina Center for Nanoscale Materials. A.C. and M.G. were 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.

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