1. INTRODUCTION

The discovery of carbon nanotubes in 1991 has stimulated considerable interest in the investigation of the physical and mechanical properties of their novel materials and their potential technological applications. Results of theoretical modeling\(^1\)–\(^5\) and experimental measurements\(^6\)–\(^9\) have confirmed that carbon nanotubes possess exceptional properties, such as high stiffness and strength, the ability to sustain large elastic strain, and high thermal and electric conductivity. These properties as well as their high respect ratio and low density suggest that carbon nanotubes may hold promise as the reinforcing phase for nanocomposites.

Reports on the improvement in stiffness and strength,\(^10\)–\(^14\) electric conductivity and electrostatic charging behavior,\(^15\)\(^,\)\(^16\) and light-emitting characteristics\(^17\) due to the addition of carbon nanotubes in polymeric matrix materials have demonstrated the promise of nanotube composites. More specifically, Schadler et al.\(^10\) reported a 20% increase in both tensile and compressive moduli of an epoxy matrix due to the dispersion of 5 wt% of multiwalled carbon nanotubes. Qian et al.\(^13\) reported a 36–42% increase in the elastic stiffness and a 25% increase in tensile strength of polystyrene with the addition of 1 wt% of carbon nanotubes. Coleman et al.\(^16\) observed that the conductivity of nanocomposites could be tailored by varying the nanotube concentration. Ajayan et al.\(^18\) demonstrated the potential of polymer-based flat-panel displays using a transparent nanotube composite with light-emitting properties. A recent review of nanotube-based composites can be found in Ref. \(^19\).

Two important factors need to be considered for the effective utilization of nanotubes as reinforcements in composites. First, the uniform dispersion and orientation alignment of nanotubes within a matrix are crucial. The agglomeration of carbon nanotubes into bundles due to van der Waals interaction causes difficulties in their dispersion in a matrix material.\(^20\) In partially dispersed bundles, the slipping between nanotubes that are not bonded to the matrix reduces the performance of the composite. In addition, the aggregate of nanotubes reduces the aspect ratio of the reinforcement. The second factor that needs to be considered is the efficiency of load transfer across the nanotube/matrix interface as affected by the interfacial bonding.\(^10\) To take full advantage of the exceptional stiffness and strength of carbon nanotubes, a high degree of interfacial bonding is desirable.

Regarding dispersion and alignment of nanotubes, various attempts have been made,\(^21\)–\(^29\) and well-dispersed and well-aligned nanotube-reinforced composites are now feasible.\(^24\),\(^27\)–\(^29\) On the other hand, the interfacial bonding issue appears to be equally challenging. The major mechanisms of load transfer for traditional fiber-reinforced polymer composites include mechanical interlocking, chemical bonding, and weak van der Waals bonding between the fiber and the matrix. These mechanisms may also be active in nanotube-reinforced polymer composites. The following are some of the interfacial related observations. The transmission electron microscopy study of Ajayan et al.\(^18\) indicated weak interfacial bonding between the nanotubes and resin matrix. The measurements of Schadler et al.\(^10\) showed better load transferring efficiency when the composites are under compression rather than tension. Bower et al.\(^30\) examined the fracture surfaces of nanotube/polymer composites stretched at a constant rate and concluded that a high density of carbon nanotubes protruded from the fracture surface, but adherence of the polymer appeared in

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*Author to whom correspondence should be addressed.*
most of the nanotubes. In some cases, the entire surface of the nanotube was covered with a layer of polymer.

In the study of carbon-nanotube/polymethyl methacrylate composites, Jia et al.\textsuperscript{31} showed the possibility of existence of carbon-carbon bonds between the nanotube and the matrix. Lordi and Yao\textsuperscript{32} examined the factors governing interfacial adhesion in nanotube-based composites from the molecular mechanics viewpoint. The binding energies and frictional forces were found to play only a minor role in determining the strength of the interface. The key factor in forming a strong bond at the interface is having a helical conformation of the polymer chain around the nanotube. Wagner et al.\textsuperscript{33} examined stress-induced fragmentation of multiwalled carbon nanotubes in polymer films. From estimated values of nanotube axial normal stress and elastic modulus, they concluded that the nanotube/polymer interfacial shear stress is on the order of 500 MPa and higher. This value is an order of magnitude higher than the stress-transfer ability of current advanced composites.\textsuperscript{39}

It is well known that the efficiency of load transfer depends on the interfacial shear stress between the reinforcement phase and the matrix. A high interfacial shear stress will transfer the applied load to the fiber over a short distance, whereas a low interfacial shear stress will require a longer transfer length. Covalent bonding can result in more efficient load transfer than van der Waals interactions. This is one of the reasons that some research efforts have been devoted to the functionalization of carbon nanotubes to facilitate the formation of covalent bonds between nanotubes and the matrix.\textsuperscript{34, 35}

Despite the various studies conducted on interfacial bonding in nanotube/matrix composites, there is a lack of quantitative understanding of the load transfer efficiencies. The fundamental issues include the interfacial shear stress distribution, the stress concentration in the matrix in the vicinity of nanotube ends, the axial stress profile in the nanotube, and the effect of the nanotube aspect ratio on load transfer. In this article we attempt to shed some light on these issues through a stress analysis of the nanotube/matrix system. Here, the nanotube is modeled by the molecular structural mechanics method at the atomistic level. The matrix is treated as a continuum and modeled by the finite element method. The nanotube/matrix interface is assumed to be bonded either perfectly or by van der Waals interactions. The objective of this article is to investigate the stress distributions in the nanotube and the polymer matrix and then to assess the effect of interfacial load transfer in nanotube/polymer composites. The rule-of-mixture for the effective composite elastic modulus is validated to establish confidence in the modeling work.

2. COMPUTATIONAL MODELS OF NANOTUBE/POLYMER COMPOSITE

Two cylindrical unit cells, as shown in Figure 1, are chosen as computational models. Figure 1a is for the continuous reinforcement model, in which the length of the nanotube is assumed to be the same as the length of the surrounding polymer matrix. Figure 1b is for the discontinuous reinforcement model in which the nanotube is entirely embedded in the matrix. The long-tube unit cell is used for computing the effective composite Young’s modulus under the isostrain assumption. The short-tube unit cell is used for revealing the stress distribution in the composite.

In the study of traditional fiber composites, the approach is to first examine the properties of the constituent phases separately and then combine them to assess the synergy. The fiber and matrix materials are often assumed to be isotropic and homogeneous, and the formation of interphase is taken into account in a multiphase model.\textsuperscript{36} However, in a nanotube/polymer composite, the characteristic of the reinforcement phase, unlike the usual fiber material, is highly size/structure dependent. Thostenson and Chou\textsuperscript{29} characterized extensively multiwalled carbon nanotubes for reinforcing a polystyrene matrix material. Both random and aligned nanotube composites were investigated. It was concluded that the nanotube reinforcement efficiency is highly sensitive to the diameter, wall thickness, and density of the nanotubes, and there is a broad distribution of the structures of the nanotubes in the composite. The findings of Thostenson and Chou\textsuperscript{29} and many other studies pertaining to the mechanical properties of carbon nanotubes\textsuperscript{2, 3, 8, 9} underscore the necessity to account for the atomistic structures of nanotubes in the modeling of their composites.

The polymeric matrix material is too formidable to model the whole matrix region at the atomistic scale. Although with current computing power the simulation of both the nanotube and the matrix at the atomistic scale has been attempted,\textsuperscript{37, 38} this kind of simulation is very time-consuming because the volume of the matrix is much greater than that of the reinforcement. As a sensible alternative, we treat the polymer matrix as a continuous medium. Therefore, it is necessary to perform multiscale modeling and to establish a linkage between modeling at the nano-
scale and the macroscale. Several multiscale modeling techniques, coupling atomistic and continuum approaches, have been proposed and implemented. However, a general computational technique bridging the nanoscale with the macroscale for nanocomposites is still not available.

2.1. Modeling of Carbon Nanotubes

Among the modeling techniques for nanostructured materials, the molecular dynamics approach has been most frequently adopted by researchers. However, for stress analysis of nanotube/polymer composites, the application of molecular dynamics for modeling of the nanotube is unnecessary because the task is essentially a static problem. To facilitate the simulation of the elastic behavior of nanocomposites, it is desirable to develop computationally efficient techniques to account for the atomistic structure of nanotubes but also be able to bridge length scales from atomistic to continuum. Toward this end, the molecular structural mechanics approach has been developed by the authors. The carbon nanotubes are assumed to be single-walled, zigzag, or armchair type without caps at the ends.

The concept of molecular structural mechanics originated from the observation of geometric similarities between nanoscopic fullerenes and macroscopic frame structures. The term fullerene was first used to describe the \( \text{C}_{60} \) molecule, a spherical carbon molecule with hexagonal and pentagonal faces. This term, named for the architect R. Buckminster Fuller and now used to describe all cage-like allotropes of carbon, refers particularly to the geometric similarities between the \( \text{C}_{60} \) molecule and geodesic domes. From the characteristics of these nanostructured molecules, it is logical to anticipate that there may be potential relationships between fullerenes and macroscopic engineering structures. Using concepts of molecular mechanics, we have bridged the vast differences in length scales of these structures based on the concept of energy equivalence.

In a carbon nanotube, each atom is bonded together covalently with its three nearest neighbors. When a nanotube is subjected to external forces, the positional changes of atomic nuclei are constrained by the covalent bonds. If a nanotube is viewed as a space frame with "beams" connecting the carbon atoms, its deformation can be considered to be similar to that of a frame structure composed of connecting beams. In essence, we model the covalent bond between carbon atoms by an equivalent structural beam. Based on the energy equivalence between local potential energies in computational chemistry and elemental strain energies in structural mechanics, we can determine the tensile resistance, flexural rigidity, and torsional stiffness of the equivalent beam. Once these beams are assembled to form a nanotube, the computationally efficient structural mechanics technique can be readily used to solve the resulting nanotube deformation problem.

The energy equivalence is schematically shown in Figure 2. From the viewpoint of molecular mechanics, the general expression of total steric potential energy is a sum of energies due to valence or bonded interactions and non-bonded interactions:

\[
U = \sum U_r + \sum U_\phi + \sum U_\psi + \sum U_{\text{vdw}} \tag{1}
\]

where \( U_r, U_\phi, U_\psi, \) and \( U_{\text{vdw}} \) are for bond stretching, bond angle bending, dihedral angle torsion, out-of-plane torsion, and van der Waals interactions, respectively. From a structural mechanics viewpoint, the deformation of a space frame results in the change of strain energy. The strain energy for a beam element is given by:

\[
U = \sum U_A + \sum U_M + \sum U_T + \sum U_Y \tag{2}
\]

where \( U_A, U_M, U_T, \) and \( U_Y \) are strain energies for axial tension, bending, torsion, and shear force, respectively.

If the equivalent beam is assumed to be of round section, then only three stiffness parameters, that is, the tensile resistance \( EA \), the flexural rigidity \( EI \), and the torsional stiffness \( GJ \), need to be determined for deformation analysis. By considering the energy equivalence between Equations (1) and (2), a direct relationship between the structural mechanics parameters and the molecular mechanics force field constants can be established, that is,

\[
\frac{EA}{L} = k_r, \quad \frac{EI}{L} = k_\phi, \quad \frac{GJ}{L} = k_\psi \tag{3}
\]

where \( k_r, k_\phi, \) and \( k_\psi \) are the force field constants in molecular mechanics, and \( L \) is the length of the equivalent beam. Then, following the procedure of the structural mechanics technique, the static or dynamic problems of carbon nanotubes can be readily solved.

2.2. Modeling of Polymer Matrix

By treating the polymer matrix as a continuum, the finite element method is adopted for modeling its deformation. As shown in Figure 1, the matrix phase in our computa-
tional models is in three-dimensional space. Thus, two kinds of three-dimensional finite elements are used in the meshing of the matrix. One is the three-dimensional 20-nodes isoparametric cubic element (Fig. 3a) and the other is the three-dimensional 15-nodes isoparametric wedge-shaped element (Fig. 3b). The 20-nodes elements are used in the circumferential region surrounding the nanotube. The 15-nodes elements are used in the regions directly above and below the nanotube (Fig. 1b).

3. INTERFACE OF NANOTUBE AND POLYMER MATRIX

Here, we consider two limiting cases in interfacial load transfer capability. The case of low interfacial load transfer is approximated by the van der Waals interface. The case of high interfacial load transfer is simulated by a perfect interface, which may exist in a covalently bonded nanotube/matrix interface.34, 35

3.1. Interface with van der Waals Interactions

For simulations of van der Waals interactions at the interface, the truss rod model is adopted, which was first developed for simulating the van der Waals forces between neighboring atomic layers of a multiwalled carbon nanotube.47 In this model, based on the Lennard-Jones “6–12” potential,53 the van der Waals force between interacting atoms is given by

\[ F(r) = -\frac{dU(r)}{dr} = 24 \frac{\varepsilon}{\sigma} \left[ \left( \frac{\sigma}{r} \right)^{13} - \left( \frac{\sigma}{r} \right)^{7} \right], \]  

where \( r \) is the interatomic distance and \( \varepsilon \) and \( \sigma \) are the Lennard-Jones parameters. For carbon atoms the Lennard-Jones parameters are \( \varepsilon = 0.0556 \text{ kcal/mole} \) and \( \sigma = 3.4 \text{ Å} \).54

The load-displacement curve of the truss rod consists of two distinct stages in loading and unloading (Fig. 4) in reflecting the highly nonlinear nature of van der Waals interactions. The load-displacement curve of the truss rod is opposite to that of the van der Waals force. The reason is that the van der Waals force is an intrinsic force between the interacting particles, whereas the load-displacement relation indicates that an external load is applied to the truss rod to overcome the van der Waals force. Thus, the prefix “anti” is attached to the terms “attraction” and “repulsion” to show this relationship. The characteristics of the load-displacement curve brings about some numerical difficulties in the simulation. In this article, we adopt the generalized displacement control method55 for simulating the nonlinearity of the truss rod. This method has been demonstrated to be accurate and numerically stable at the critical and snap-back points.

At the nanotube/matrix interface, the activation of a truss rod is determined by the distance between an atom in the nanotube and a node in the finite element. For convenience in computation, we only consider the van der Waals interactions between the nanotube and the surface of the polymeric matrix immediately adjacent to the nanotube. This assumption may tend to underestimate the load transfer capability of the nanotube/polymer interface. The center of the atoms in the single-walled nanotube is assumed to be located in the midsection of the tube thickness (as shown in Fig. 5a), which is assumed to be 0.34 nm. We have noticed the various assumptions of wall thickness, such as 0.34 nm,4 0.066 nm,5 and 0.0894 nm.56 A detailed discussion of this issue has been given by Yakobson and Avouris.57 Considering the relationship between graphite...
and multiwalled carbon nanotubes and for the purpose of comparing their elastic properties, we assumed the thickness of a single-walled carbon nanotube to be the same as the interlayer spacing of graphite (0.34 nm). The inner surface of the polymer matrix is assumed to be located at the same position as the outer surface of the nanotube. If the distance between an atom in the nanotube and a node in the inner surface of the matrix is less than 2.5 σ, a truss rod is activated. This criterion is based on the fact that the van der Waals force from the Lennard-Jones potential is negligible when the distance between atoms is beyond 2.5 σ as shown in Figure 4.

3.2. PERFECT INTERFACE

For a perfectly bonded interface, it is still assumed that the outer surface of the nanotube coincides with the inner surface of the polymer matrix. However, for matching the atoms in the nanotube and the nodes in the finite elements, the center of an atom in the nanotube is assumed to be located on the outer surface (as shown in Fig. 5b), not in the center of the tube wall. The corner nodes of finite elements in the matrix coincide with atoms in the nanotube but the mid-side nodes of finite elements are left suspending for the purpose of keeping the matrix in a cylindrical shape.

4. RESULTS AND DISCUSSION

Using the molecular structural mechanics approach and the finite element method, a computational modeling of a continuous nanotube and a discontinuous nanotube reinforced polymeric matrix composite has been carried out. The Young’s modulus and Poisson ratio of the polymer matrix are taken as 2.41 GPa and 0.35, respectively, for simulating an epoxy polymer. The nanotube is assumed to be the zigzag type.

4.1. Effective Young’s Moduli of Nanotube/Polymer Composites

The effective Young’s moduli of nanotube/polymer composites are analyzed using the long-tube computational model. The nanotube/polymer interfacial bonding is assumed to be a van der Waals interaction. A tensile isostrain condition is also assumed. Two maximum applied strains, 0.103% and 0.414%, are considered. The outer radius of the nanotube is taken as 4.71 Å, and the outer radius of the polymer matrix is 5 times the nanotube outer radius. The selection of the size of the polymer matrix is based on the consideration of eliminating the local effect of interface on stress distribution in the polymer matrix.

The computational results are listed in Table I, where the sectional areas of the nanotube and the matrix are calculated as following

\[ A_n = \pi (R_n^2 - (R_n - 3.4)^2) \]  

(5a)

where \( R_n \) and \( R_m \) represent the outer radii of the nanotube and the polymer matrix, respectively. It is found that the majority of the axial force is carried by the nanotube, although the gross volume fraction of the nanotube \( V_{nt} = A_{nt} / (A_{nt} + A_m) = 3.4\% \) is much less than that of the matrix \( V_m = 1 - V_{nt} = 96.6\% \). The effective composite axial Young’s modulus is calculated from the ratio of the sum of total forces in the matrix and the nanotube to the product of total sectional area and applied strain.

For continuous fiber-reinforced composites, it is well known that the effective axial Young’s modulus follows the rule-of-mixtures, that is,

\[ E_c = E_f V_f + E_m V_m \]  

(6)

where \( E \) and \( V \) stand for Young’s modulus and volume fraction, respectively, and subscripts \( c, f, \) and \( m \) represent composite, fiber and matrix, respectively. By assuming the Young’s modulus of carbon nanotubes to be 1000 GPa and the nanotube volume fraction to be ∼3.4%, the effective Young’s modulus of nanotube/polymer composite predicted from Equation (4) would be 36.46 GPa, which is in very good agreement with that predicted from the present computations. It should be noted that the results of Table I are obtained without the need of preassuming the elastic properties of the nanotube, which was automatically generated from the molecular structural mechanics analysis.

4.2. Nanotube/Polymer Interfacial Shear Stresses

The stress distributions in the nanotube/polymer composite are analyzed for the short-tube computational model (Fig. 1b) under both isostrain and isostress loading conditions. Different nanotube aspect ratios as well as the limiting interfacial conditions, a van der Waals interface, and a perfect interface are examined. Figures 6 and 7 illustrate the computational results of the interfacial shear stress. In these figures, the stresses are normalized by either the uniform applied stress (isostress case) or the applied strain multiplied by the Young’s modulus of the polymer (isostrain case). Because the stress distribution is axially symmetric with respect to the nanotube centerline, only one quarter of the matrix material is shown in a radial section.
through the nanotube centerline. The dimensions of the section are also indicated.

Figure 6 displays the distributions of normalized shear stress in a quarter of the matrix material for a perfect interface and a van der Waals interface. It is observed that the maximum shear stresses occur at the vicinity of nanotube ends. The shapes of shear stress contours for the perfect interface and van der Waals interface cases are similar, but the maximum normalized shear stress in the former case is roughly twice as much as that of the latter case.

Figure 7 shows the profile of normalized shear stress for three nanotube aspect ratios with the two interfacial conditions discussed above and isostress and isostrain loading conditions. It can be seen that, for the same loading condition, there are only small differences between the maximum stresses for different nanotube aspect ratios. However, because the region of shear action is larger for a larger aspect ratio, longer nanotubes possess higher load-carrying capability, as expected. Under the same loading condition, the shear stresses due to a perfect interface are much larger than those due to a van der Waals interface. Also, under the same interface assumption and the same nanotube aspect ratio, the shear stresses in the matrix under the isostrain loading condition are higher than those under the isostress loading condition.

**Fig. 6.** The shear stress distributions in a polymer matrix (zigzag single-walled carbon nanotube: radius = 4.71 Å, aspect ratio = 12.82). (a) Perfect interface, isostrain, max = 2.78;p (b) van der Waals interface, isostrain, max = 1.13; (c) perfect interface, isostress, max = 1.15; (d) van der Waals interface, isostrain, max = 0.68.

**Fig. 7.** The effect of nanotube aspect ratio on the shear stress profile (zigzag single-walled carbon nanotube: radius = 4.71 Å): (a) perfect interfacial interface; (b) van der Waals interfacial interface.
4.3. Axial Normal Stress Concentrations in the Nanotube and Polymer Matrix

Figure 8 shows the axial normal stress distributions in the polymeric matrix under isostrain and isostress loading conditions. It is observed that there are stress concentrations in the vicinity of the nanotube ends for both types of interface, which could be the sites of microcracking initiation in the matrix material. The nature of stress concentrations in nanotube/polymer composites is similar to that in short fiber-based composites. The magnitude of tensile stress concentrations under the isostrain condition is again higher than that in the isostress condition.

Figure 9 displays the axial stress distributions in the nanotube under the isostrain condition. The tensile stress along the tube length (normalized by tube diameter) is symmetrically distributed with the maximum stress appearing at the middle section of the tube. Compared with Figure 8, the maximum stress in the nanotube is much higher than that in the polymer matrix. Also, the maximum stress in the case of a perfectly bonded interface is larger than that in a van der Waals interface. Although strength of single-walled nanotubes as high as 50 GPa was reported, the stress concentration may cause failure of nanotubes due to preexisting defects as indicated in some experiments showing that nanotubes in nanotube/polymer composites were broken in tension testing.

In our computational models the nanotubes are assumed to be without end caps. This is mainly for the convenience in finite element meshing, and it should give the upper bound in stress concentration. However, hemispherical end caps often exist in nanotubes, and stress concentrations at the nanotube ends in these cases may not be as serious as our predictions in this article.

5. CONCLUSIONS

The interfacial load transfer in carbon nanotube/polymer composites has been analyzed by combining the atomistic molecular structural mechanics approach and continuum finite element method. Two kinds of interfacial conditions, that is, perfect interface and van der Waals interface, are considered. The results confirm the validity of the rule-of-mixtures prediction for axial elastic modulus at the nanoscale. The stress concentrations in the nanotube as well as in the matrix material have been identified for various load-
ing conditions, nanotube aspect ratios, and interfacial conditions. The knowledge gained in the present study forms the base for further multiscale analysis of nanotube fracture, interfacial debonding, microcrack extension, and failure of nanotube-based composites. The methodology developed is applicable to both polymer and ceramic composites in which the matrix deformation is in the elastic range.

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References and Notes


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