Multiscale micromechanical modeling of the constitutive response of carbon nanotube-reinforced structural adhesives

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Abstract

Appropriate formulations are developed to allow for the atomistic-based continuum modeling of nano-reinforced structural adhesives on the basis of a nanoscale representative volume element that accounts for the nonlinear behavior of its constituents; namely, the reinforcing carbon nanotube, the surrounding adhesive and their interface. The newly developed representative volume element is then used with analytical and computational micromechanical modeling techniques to investigate the homogeneous dispersion of the reinforcing element into the adhesive upon both the linear and nonlinear properties. Unlike our earlier work where the focus was on developing linear micromechanical models for the effective elastic properties of nanocomposites, the present approach extends these models by describing the development of a nonlinear hybrid Monte Carlo Finite Element model that allows for the prediction of the full constitutive response of the bulk composite under large deformations. The results indicate a substantial improvement in both the Young's modulus and tensile strength of the nano-reinforced adhesives for the range of CNT concentrations considered.

1. Introduction

It has been recognized for some time that the mechanical properties of polymeric materials can be engineered by fabricating composites that are comprised of different volume fractions of one or more reinforcing phases. A number of techniques have been considered to improve the mechanical properties of structural adhesives. They included the addition of carbon, nylon or glass micro-fibers, rubber and liquid rubber precipitates, reactive ductile diluents and inorganic hybrid particles, among others. Whilst some improvements in bond properties have been observed (Kawashita et al., 2008; Takemura, 2007), these additives also led to reductions in high temperature service capabilities, low impact strength, and poor shrinkage characteristics (Petrie, 2006). As time has progressed, practical realization of composites has begun to shift from micro-scale composites to nanocomposites, taking advantage of the unique combination of mechanical and physical properties of nanofillers (fillers with a characteristic dimension below 100 nm). There are a number of advantages associated with dispersing nanofillers in polymeric materials. While some credit can be attributed to the intrinsic properties of the fillers, most of these advantages stem from the extreme reduction in filler size combined with the large enhancement in the specific surface area and interfacial area they present to the matrix phase. In addition, whereas traditional composites use over 40 wt% of the reinforcing phase, the dispersion of just a few weight percentages of nanofillers into polymeric matrices could lead to dramatic changes in their mechanical properties with added functionalities.

In this work, we propose to reinforce the adhesive layer through the homogeneous dispersion of only a small fraction of carbon nanotubes (CNTs). CNTs are regarded as one of the most promising reinforcement materials for the next generation of high-performance structural and multifunctional composites (Endo et al., 2004). These molecular scale tubes of graphitic carbon have outstanding mechanical, thermal and electrical properties. In fact, some CNTs are stronger than steel, lighter than aluminum, and more conductive than copper (Moniruzzaman and Winey, 2006). Theoretical and experimental studies have shown that CNTs exhibit extremely high tensile modulus (1 TPa) and strength (150 GPa). In addition, CNTs exhibit high flexibility, low density (1.3–1.4 g/cm$^3$), and large aspect ratios (1000 s). Due to this unique combination of physical and mechanical properties, CNTs have emerged as excellent candidates for use as tailoring agents in polymeric materials to yield the next generation nanocomposites.

The design and fabrication of nano-reinforced adhesive composites requires rigorous characterization and analysis. Excellent
nanotube tube properties do not necessarily translate into the same properties for the bulk composite. Several issues pertaining to the alignment, dispersion, aspect ratio, orientation, and load transfer need to be optimized in order to achieve the best properties of the composite. Two approaches have generally been adopted in treating this class of materials, namely, experimental and theoretical. Although there exists plenty of notable experimental efforts, these are severely hindered by the technical difficulties encountered during the manipulation, fabrication, and processing of CNTs and their composites. As such, there exists significant variability amongst experimental results and no set standards exist to streamline the manufacturing process. This has motivated the use of theoretical and computational approaches to predict the effective mechanical properties of bulk nano-reinforced composite systems.

Recently, an interfacial cohesive law has been developed by Jiang et al. and applied to study the interaction between CNT walls (Lu et al., 2007) and CNT polymer composites (Jiang et al., 2006). The cohesive law was used in a micromechanical analysis to predict the stress–strain behavior of CNT polyethylene composites (Tan et al., 2007). The predicted stress–strain curves displayed an intermittent decrease in both stress and strain due to the interface softening behavior displayed in the cohesive law. The studies showed that CNTs indeed improve the mechanical behavior of composites at small strain. However, the improvement disappears at relatively large strain because the debonded nanotubes behave like voids in the matrix and may even weaken the composite.

Chen and Liu (2004) and Liu and Chen (2003) evaluated the effective mechanical properties of CNT polymer composites using a square representative volume element (RVE) based on continuum mechanics. They were able to extract the effective elastic mechanical properties of both discontinuous and continuous CNT polymer composites by analyzing the RVE under a variety of loading conditions. They found that with the addition of only about 3.6% volume fraction of the CNTs, the stiffness of the composite in the CNT axial direction can increase as much as 33% for the case of long CNT.

Lusti and Gusev (2004) used finite element methods to investigate the effect of CNT orientation, aspect ratio and volume fraction on the effective elastic properties of CNT polymer composites. They considered fully aligned, two-dimensional random in-plane and three-dimensional random orientation states at various CNT concentrations. In their study the CNTs were modeled as massive cylinders which were randomly distributed in a computational cell using a Monte Carlo (MC) algorithm. Their results show that fully aligned nanotubes lead to a significant enhancement in the longitudinal properties whereas two dimensional random in-plane and three-dimensional randomly oriented nanotubes increase the effective properties considerably less, but equally, in more than one direction.

Several micromechanical schemes including sequential homogenization and various extensions of the Mori–Tanaka method were compared in a recent study of the elastic properties of SWCNT-based polymers by Selmi et al. (2007). The comparative study showed that for all composite morphologies considered (fully aligned, two-dimensional in-plane random orientation, and three-dimensional random orientation) the two-level Mori–Tanaka/Mori–Tanaka approach delivered the best predictions when validated using both experimental and finite element (FE) results.

The above micromechanical investigations of the effective mechanical properties of CNT-reinforced composites typically employ linear analytical formulations such as the Mori–Tanaka scheme and its derivatives. These investigations certainly assist in understanding the effects of such parameters as CNT concentration, aspect ratio, and orientation upon the linear elastic properties of the bulk composite. However, it is also of interest to the scientific community to understand how these parameters govern the full constitutive response of the nanocomposite subject to large deformations. In this study, we present an initial prediction of the full constitutive response of the bulk nano-reinforced adhesive under large tensile deformations. Appropriate formulations are developed to allow for the atomistic-based continuum modeling of nano-reinforced structural adhesives on the basis of a nanoscale RVE. The newly developed RVE is then used with analytical and computational micromechanical modeling techniques to investigate the homogeneous dispersion of the reinforcing element into the adhesive upon both the linear and nonlinear properties. A schematic of this approach is provided in Fig. 1. This approach was also adopted in our earlier works (Meguid et al., 2010) in the analysis of the effective elastic moduli of nanocomposites containing aligned and randomly distributed CNTs. However, there are a number of fundamental differences in the present approach that are worth noting. First, the RVE is formulated for a specific two-component epoxy system with homogenous material properties. Unlike our previous publication which focused on a generic polymer with a discrete and aligned chemical structure. Secondly, in the current micromechanical study we divert from our previous work by assuming transversely isotropic material symmetry for the reinforcing RVE. Finally, in the present computational approach, we extend our previous efforts by adopting traditional continuum FE concepts coupled with MC techniques to develop large scale three-dimensional micromechanical models that can be used to predict the resulting stress and strain fields in the nanocomposite for large deformations.

2. Atomistic-based continuum modeling

A three-dimensional nonlinear representative volume element (RVE) is developed to study the nano-reinforced adhesive system. The RVE consists of the reinforcing CNT, the surrounding polymer matrix, and the CNT-epoxy interface, as depicted in Fig. 1. Due to the inherent nano-scale involved in simulating CNT structures, an atomistic description is incorporated. First, the carbon–carbon (C–C) covalent bonds in the CNT structure are described using the Modified Morse interatomic potential. Secondly, the atomic van der Waals (vdW) interactions between the atoms in the CNT and the atoms in the adhesive matrix are described using the Lennard–Jones (LJ) interatomic potential. This description implies the assumption of a non-bonded interfacial region. The atomistic-based continuum (ABC) multiscale modeling technique is used to model the components of the RVE. The approach adopted here extends the earlier work of Wernik and Meguid (2011). However, for the sake of completeness, we provide a brief outline of the method detailed in our earlier work.

Fundamental to the proposed concept is the notion that a CNT is a geometrical space-frame-like structure and the primary bonds between two nearest-neighboring atoms act like load-bearing beam members as depicted in Fig. 2. As in traditional FE models, nodes are used to connect the beam elements to form the CNT structure. In this case, the nodes represent the carbon atoms and are defined by the same atomic coordinates. We adopt the Modified Morse interatomic pair potential with an added angle-bending term to describe the atomic interactions in the CNT. The parameters used for the potential in this study are the same as those adopted by Belytschko et al. (2002), and are presented in Table 1. The Modified Morse potential is given by:

\[ E = E_s + E_b \]  
\[ E_s = D_s \left( \left(1 - \exp^{-b(r-\sigma)^2}\right) - 1 \right) \]

where:
- **E**: Energy
- **E_s**: Morse energy
- **E_b**: Bending energy
- **D_s**: Elastic constant
- **r**: Distance between atoms
- **\sigma**: Equilibrium bond length
- **b**: Morse parameter

For the bending term, the parameter \( D_b \) is given by

\[ D_b = \frac{3}{2} \left(1 - \exp^{-b(r-\sigma)^2}\right) \]
where \( r_0 \) is the initial bond length, \( \theta_0 \) is the initial angle between adjacent bonds, \( D_e \) is the dissociation energy, \( \beta \) is a constant which controls the 'width' of the potential, and \( k_h \) and \( k_{\text{sextic}} \) are the angle-bending force constants.

Nonlinear rotational spring elements are used to account for the angle-bending component, while beam elements are used to represent the stretching component of the potential. In order to ensure an appropriate connectivity and transmission of moments among adjacent beam elements, the rotational springs were defined between coincident nodes with coupled translational and rotational degrees of freedom. To describe the behavior of the beam and rotational spring elements, we first derive material models for each which accurately represents the characteristics of the Modified Morse potential. First, by deriving the stretching potential (Eq. (2)) with respect to the change in bond length and by utilizing the following relationship,

\[
e = \frac{r}{r_0}
\]

we can arrive at the expression:

\[
F = 2\beta D_e \left( 1 - \exp\left( -\beta r \right) \right) \exp\left( -\beta r \right)
\]

which represents the force required to stretch a C–C bond. This expression is used to describe the material behavior of the beam elements. Likewise, differentiating the angle-bending component of the potential (Eq. (3)) with respect to the change in rotation, we can arrive at the following expression:

\[
M = k_h \Delta \theta \left[ 1 + 3 k_{\text{sextic}} (\Delta \theta)^4 \right]
\]

where \( E_l = \frac{1}{2} k_h (\theta - \theta_0)^2 \left[ 1 + k_{\text{sextic}} (\theta - \theta_0)^4 \right] \) (3)

which represents the moment required to bend neighboring bonds. Again, this expression is used to define the stiffness of the rotational spring elements throughout the simulation.

The Lennard–Jones interatomic potential is used to describe the vdw interactions at the CNT/polymer interface. The LJ potential is defined as

\[
E_l = 4\mu \left( \frac{\psi}{r} \right)^{12} - \left( \frac{\psi}{r} \right)^{6}
\]

where \( \mu \) is the potential well depth, and \( \psi \) is the hard sphere radius of the atom or the distance at which \( E_l \) is zero, and \( r \) is the distance between the two atoms. In this study, we investigate the non-bonded interactions between the carbon atoms in the CNT and the atoms in the polymer. The LJ parameters for the interactions considered in this paper are summarized in Table 2.

We adopt the ABC technique to explicitly model each interaction across the interface using the concept of continuum elements. In this case, each atomic interaction is represented by a continuum truss rod which extends out from a carbon atom in the CNT structure to an atom in the epoxy matrix, as shown in Fig. 3. Again, by differentiating the potential with respect to the separation distance, we arrive at an expression for the vdw force between two interacting atoms:

\[
F_{\psi} = 24 \mu \left( \frac{\psi}{r} \right)^{13} - \left( \frac{\psi}{r} \right)^{7}
\]

This expression is used to determine the magnitude of the force in each interaction, which depends solely on the separation distance between the atoms and the type of atoms considered.

Table 1
Modified Morse potential parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_0 ) (m)</td>
<td>( 1.421 \times 10^{-10} )</td>
<td>( \theta_0 ) (rad)</td>
<td>2.094</td>
</tr>
<tr>
<td>( D_e ) (N m)</td>
<td>( 6.031 \times 10^{-19} )</td>
<td>( k_h ) (N m rad(^{-2}))</td>
<td>( 0.876 \times 10^{-18} )</td>
</tr>
<tr>
<td>( B ) (m(^{-1}))</td>
<td>( 2.625 \times 10^{10} )</td>
<td>( k_{\text{sextic}} ) (rad(^{-4}))</td>
<td>0.754</td>
</tr>
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</table>

Table 2
Lennard–Jones potential parameters.

<table>
<thead>
<tr>
<th>LJ interaction</th>
<th>( \mu ) (J)</th>
<th>( \psi ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon–carbon (C–C)</td>
<td>( 3.89 \times 10^{-22} )</td>
<td>0.34</td>
</tr>
<tr>
<td>Carbon–hydrogen (C–H)</td>
<td>( 4.44 \times 10^{-22} )</td>
<td>0.32</td>
</tr>
<tr>
<td>Carbon–oxygen (C–O)</td>
<td>( 4.90 \times 10^{-22} )</td>
<td>0.32</td>
</tr>
<tr>
<td>Carbon–nitrogen (C–N)</td>
<td>( 4.48 \times 10^{-22} )</td>
<td>0.33</td>
</tr>
</tbody>
</table>
To model the surrounding epoxy matrix, a specific two-component epoxy structural adhesive is used based on a diglycidyl ether of bisphenol A (DGEBA) and triethylene tetramine (TETA) formulation. This adhesive is a virgin epoxy with no added fillers. The addition of fillers such as those used in typical aerospace adhesives may serve to impede on the mechanical reinforcement of the CNTs. Tension tests according to ASTM D638 were conducted on cured dogbone test specimens to determine the average constitutive response of the cured adhesive. The measured stress–strain response is input as multi-linear elastic material property in the present model and is depicted in Fig. 4. The Young’s modulus and Poisson’s ratio of the epoxy matrix is taken to be 1.07 GPa and 0.28, respectively. The epoxy is modeled using higher ordered 3-D, 10-node solid tetrahedral elements with quadratic displacement behavior. The element is defined by 10 nodes having three degrees of freedom at each node: translations in the nodal x, y, and z directions. Throughout the analysis, the volume of the polymer is varied in order to investigate the effect of the CNT volume fraction on the effective mechanical properties of the nano-reinforced epoxy system.

It becomes important to establish the appropriate level of nodal refinement in the surrounding adhesive region as this is an important parameter which governs the number of vdW interactions across the interface, or equivalently, the number of truss rod elements. Ideally, molecular dynamic (MD) simulations would be employed to establish the correct atomic morphology of the adhesive from which the atomic positions of the atoms can be extracted and used to define the nodal locations in the continuum model. Without first employing MD simulations to determine the exact morphology of the polymer chains in their lowest energy state, it is rather difficult to establish the exact location of the atoms in the near vicinity of the CNT. However, the complex atomic composition of the chosen DGEBA/TETA formulation makes it extremely difficult to model in an MD framework. In fact, the MD modeling of complex polymers has been a challenging task for the scientific community due to the number of parameters that influence the predicted structure. These include the governing interatomic potentials, the polymer system being investigated, the chosen time-stepping algorithms, how the boundary conditions are applied and the energy minimization techniques. However, the research community has succeeded in modeling relatively simple polymer systems. These include polyethylene (PE), poly-\(m\)-phenylene- \(n\)-vinylene (PMoPV), polystyrene (PS), polyamide-6 (PA6), polymethyl methacrylate (PMMA), and polyaniline (PANI) to name a few. However, emphasis has been placed on the former due to its relatively simple atomic composition of hydrogen and carbon atoms with well-established bonding interactions (Perpete and Laso, 2006). Therefore, to avoid the computational limitations of MD, the atomic density of the two-component epoxy system is determined using simple stoichiometric calculations. From this, the number of nodes in the polymer representation can be determined and used to define the correct number of truss rods across the interface.

The chosen epoxy system consists of a base resin and hardening agent. The base resin exhibits the atomic structure depicted in Fig. 5, where \(n\) is approximately 0.15. This atomic structure corresponds to a molecular mass of approximately 383.07 g/mol, with a molecular formula of \(C_{23.67}H_{38.32}O_{4.5}\). The density of the resin is 1.16 g/cm\(^3\). The atomic structure of the curing agent is depicted in Fig. 6. It has a corresponding molecular mass of 146.23 g/mol, with a molecular formula of \(C_{9.3}H_{14.0}N_{4.5}\) and a density of 0.93 g/cm\(^3\). The mix ratio between the base resin and curing agent is 2 parts to 1 parts, respectively. Therefore a sample of the cured epoxy would have a density of approximately 1.09 g/cm\(^3\), with an average polymer chain composed of \(C_{21.7}H_{29.5}O_{3.5}N_{0.45}\). This corresponds to an average polymer chain mass of 356.01 u (atomic mass units), or 5.912 \(\times\) 10\(^{-22}\) g. From this, a molecular density of 1.843 \(\times\) 10\(^{21}\) molecules/cm\(^3\), or 1.843 molecules/nm\(^3\), can be derived. Based on the above calculations, the approximate quantities of atoms present in the surrounding matrix (per cubic nanometer) are determined and provided in Table 3. From this, we can infer an approximate polymer nodal density of 99 nodes/nm\(^3\) which defines the nodal refinement level in the polymer region for the varied volumes considered.

It should be noted that the predicted polymer nodal density is only a rough estimate and is based on a number of key assumptions. For example, the above approach assumes that there are no significant secondary reactions or by-products forming during the curing process that would drastically change the average polymer composition or density. The stochastic nature of epoxies means that the density of atoms will vary, depending on how the resin and hardener interact and the curing temperature. Also, in a practical setting, the atomic density will change depending on what other constituents are mixed into the resin or hardener, and what anomalies or voids are introduced during the manufacturing of the nanocomposite. Even the most sophisticated methods of determining atomic density (such as MD simulations) would fail to account for all the possible variations.

With all the components of the RVE defined and their constitutive laws established, the RVE can be constructed by combining the individual entities. Fig. 7 depicts the RVE in its final form. The dimensions provided in the figure are for the case of maximum CNT loading where the CNT volume fraction totals 32% and for an interfacial thickness of 0.38 nm. For the sake of clarity, the interfacial truss rod representation has been omitted from all the views in Fig. 7 apart from the inset.
3. Micromechanical determination of effective mechanical properties of nanocomposites

In this section, we describe both the analytical and numerical micromechanical modeling techniques used to scale-up to the macro-level and provide an estimate of the bulk constitutive properties of the nanocomposite. We first discuss the homogenization of the RVE into a representative fiber which accurately accounts for the structure–property relationships at the nanoscale and provides a bridge to the continuum model. The Mori–Tanaka micromechanical method is derived for both unidirectionally aligned and randomly orientated CNTs. Finally, we describe the development of large-scale hybrid MC/FEA simulations used to predict the full constitutive response of the bulk nanocomposite subject to large displacements.

3.1. The representative fiber

We have introduced the concept of the RVE in which each of its constituent phases were explicitly modeled. This explicit approach is necessary because the RVE of a typical nanostructured material is on the nanometer length scale, therefore, the material is not continuous, but is an assemblage of many atoms and their interactions govern the resulting mechanical properties. However, in order to scale-up to the macro level, the RVE must be homogenized into a representative fiber exhibiting the same geometrical and mechanical characteristics such that it behaves as an equivalent continuous medium. With the RVE in place, the representative fiber can be constructed. The geometry of the linear-elastic, homogenous representative fiber is assumed to be cylindrical, similar to that of the RVE. The mechanical properties of the representative fiber are determined by equating the total strain energies of the RVE and representative fiber under identical sets of loading conditions. Examination of the RVE model reveals that it is best described as having transversely isotropic symmetry, with the plane of isotropy perpendicular to the longitudinal axis of the nanotube (Shen and Li, 2004; Montazeri et al., 2010). There are five independent material parameters required to determine the entire set of elastic constants for a transversely isotropic material. Each of the five independent parameters may be determined from a single set of boundary conditions applied to both the RVE and representative fiber. Once the mechanical properties of the representative fiber are determined, then the model can in turn be used with the appropriate micromechanical techniques to provide an estimate of the bulk effective mechanical properties of the nanocomposite for varied CNT concentrations and aspect ratios. In this way, the representative fiber acts as a vital link between atomistic and continuum scales.

3.2. Representative fiber constitutive model

The constitutive relationship of the transversely isotropic representative fiber is:

$$\sigma_{ij} = C_{ijkl} e_{kl}$$  \hspace{1cm} (8)

where $\sigma_{ij}$ and $e_{ij}$ are the stress and strain components, respectively ($ij = 1, 2, 3$), and $C_{ijkl}$ are the elastic stiffness components of the representative fiber (denoted by subscript $f$). Alternatively, Eq. (8) can be simplified by using the usual contracted notation for the elastic stiffness components and transversely-isotropic symmetry:
\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{12} \\
\sigma_{23} \\
\sigma_{31}
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{66} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{66} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{12} \\
\varepsilon_{23} \\
\varepsilon_{31}
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
0
\end{bmatrix}
\] 

(9)

For a transversely isotropic material five independent elastic properties are required to describe the complete set of elastic stiffness components. For a transversely isotropic material with a 2–3 plane of symmetry, five such properties are the longitudinal Young's modulus, \(E_l\), longitudinal shear modulus, \(C_{12}\), transverse shear modulus, \(C_{13}\), the plain-strain bulk modulus, \(K_t\), and the elastic stiffness component, \(C_{11}\). The elastic constants are related to the elastic stiffness components by:

\[
\begin{align*}
E_l &= C_{11} - \frac{2C_{12}^2}{C_{22} - C_{23}} \\
C_{12}^t &= C_{66} \\
C_{13}^t &= \frac{1}{2} (C_{22} - C_{23}) \\
K_t^t &= \frac{1}{2} (C_{22} + C_{23})
\end{align*}
\]

(10)

At this point, both the elastic constants and the elastic stiffness components are unknown. These values are determined by applying five identical sets of boundary conditions to the RVE and the representative fiber, and by subsequently equating the strain energies by adjusting the five independent elastic constants. Boundary conditions must be chosen such that they yield unique values for the independent elastic constants.

### 3.3. Boundary conditions

Five sets of boundary conditions are chosen to determine each of the five independent elastic constants such that a single property can be independently determined for each boundary condition. The displacements and tractions applied at the boundary of the RVE are generalized, respectively, by:

\[
\begin{align*}
u_i(B) &= \varepsilon_{pq} x_j \\
T_i(B) &= \sigma_{pq} n_j
\end{align*}
\]

(11)

where \(B\) is the bounding surface, \(x_j\) is defined in Fig. 8 and \(n_i\) are the components of the outward normal vector to \(B\). The generalized total strain energy of the representative fiber is

\[
\chi = \frac{V}{2} \sigma_{pq} \varepsilon_{pq} - \frac{\pi D L}{8} \sigma_{pq} \varepsilon^L
\]

(12)

where \(V, D,\) and \(L\) are the volume, diameter and length of the representative fiber, respectively.

For example, the longitudinal Young's modulus is determined by prescribing a strain along the \(x_3\) axis, \(\varepsilon_{11} = e\) with all of the shear strain components set to zero. Since a transverse Poisson contraction is allowed in this case, the transverse normal stresses are set to zero, \(\sigma_{22} = \sigma_{33} = 0\). From Eq. (11), the boundary conditions are:

\[
\begin{align*}
u_1(B) &= e x_3 \\
T_1(B) &= 0 \\
T_2(B) &= 0
\end{align*}
\]

(13)

The strain energy is:

\[
\chi = \frac{1}{8} \pi D L \varepsilon^L e^2
\]

(14)

The representative fiber strain energy, \(\chi^f\), is equated to the strain energy of the RVE subjected to the boundary conditions in Eq. (13). Since \(D\) and \(L\) are known, and \(e\) is arbitrarily chosen in determining \(\chi^f\) (in the range of small deformations), then the longitudinal Young's modulus is evaluated using Eq. (14). The boundary conditions and strain energies for each of the five independent elastic properties are summarized and listed in Table 4. Unspecified strain components are zero valued.

### 3.4. Material property summary

The five independent elastic constants and the resulting stiffness components, from Eq. (10), were determined for a representative fiber and RVE having a diameter, \(D\), of 2.4 mm, a length, \(L\), of 3.45 mm, and an applied strain, \(e\), of 0.1%. These values are listed in Table 5 and the resulting constitutive law for the transversely isotropic representative fiber is given in Eq. (20) while that of the isotropic epoxy matrix is given in Eq. (21) using the values of 1.07 GPa and 0.3 for the epoxy's Young's modulus and Poisson ratio, respectively:

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{12} \\
\sigma_{23} \\
\sigma_{31}
\end{bmatrix} =
\begin{bmatrix}
469.3 \\
7.3 \\
7.3 \\
0 \\
0 \\
0
\end{bmatrix}
\]

(20)

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{12} \\
\sigma_{23} \\
\sigma_{31}
\end{bmatrix} =
\begin{bmatrix}
2.02 \\
0.87 \\
0.87 \\
0 \\
0 \\
0
\end{bmatrix}
\]

(21)
Representative fiber independent constants and elastic stiffness components.

<table>
<thead>
<tr>
<th>Elastic constant</th>
<th>Strain energy equation</th>
<th>Boundary condition</th>
<th>Boundary displacement</th>
<th>Eqs. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f^1$</td>
<td>$\chi = \frac{1}{2} \pi D'' f' e^2$</td>
<td>$\varepsilon_{11} = \varepsilon$</td>
<td>$u_1(B) = \varepsilon$</td>
<td>[15]</td>
</tr>
<tr>
<td>$G_{1f}$</td>
<td>$\chi = \frac{1}{2} \pi D'' L f' G_{1f} e^2$</td>
<td>$\varepsilon_{12} = \varepsilon / 2$</td>
<td>$u_1(B) = \frac{\varepsilon}{2}$</td>
<td>[16]</td>
</tr>
<tr>
<td>$G_{2f}$</td>
<td>$\chi = \frac{1}{2} \pi D'' L f' G_{2f} e^2$</td>
<td>$\varepsilon_{21} = \varepsilon / 2$</td>
<td>$u_2(B) = \frac{\varepsilon}{2}$</td>
<td>[17]</td>
</tr>
<tr>
<td>$K_{f}$</td>
<td>$\chi = \frac{1}{2} \pi D'' L f' K_{f} e^2$</td>
<td>$\varepsilon_{22} - \varepsilon_{33} = \varepsilon$</td>
<td>$u_2(B) = \varepsilon$</td>
<td>[18]</td>
</tr>
<tr>
<td>$C_{11}^f$</td>
<td>$\chi = \frac{1}{2} \pi D'' L f' C_{11}^f e^2$</td>
<td>$\varepsilon_{11} = \varepsilon$</td>
<td>$u_1(B) = \varepsilon$</td>
<td>[19]</td>
</tr>
</tbody>
</table>

3.5. Micromechanical analysis using Mori–Tanaka formulations

The representative fiber accurately accounts for the structure–property relationships at the nanoscale and provides a bridge to the continuum model. With this process established, constitutive models of the effective CNT/epoxy nanocomposite can be developed by employing a micromechanical analysis using the mechanical properties of the representative fiber and the bulk epoxy matrix material given in Eqs. (20) and (21). For the composite considered in this study, the epoxy material immediately surrounding the CNT is included in the representative fiber, and it is assumed that the matrix polymer surrounding the representative fiber has mechanical properties equal to those of the bulk DGEBA/TETA epoxy. Therefore, a condition of perfect bonding between the representative fiber and the surrounding polymer matrix is assumed.

The Mori–Tanaka micromechanical method (Mori and Tanaka, 1973) is used to predict the elastic stiffness properties of the effective nanocomposite. This method has been successfully applied to transversely-isotropic inclusions by Qui and Weng (1990). Furthermore, a number of analytical efforts have employed the scheme in the prediction of the effective properties of various nanocomposites (Shady and Gowayed, 2010; Aragh et al., 2012; Jam et al., 2013). The Mori–Tanaka method allows the average stress field and overall effective stiffness of a composite with a non-dilute concentration of inclusions to be determined. Specifically, we are interested in the Mori–Tanaka solution for a two-phase composite, where the inclusion phase is randomly orientated in three dimensional space. The details of this method are not presented here but can be found in the publication by Tandon and Weng (1984). The cases of both uniformly aligned and randomly oriented representative fibers were examined in the present analysis. The representative fibers were assumed to be spheroidal in geometry for the Eshelby tensor and both the CNT and the representative fibers have the same length. It was also assumed that the CNT volume fraction was defined as the total space occupied by the CNT, including half of the interfacial region. From this, it was determined that the CNT volume fraction was 32% of the total representative fiber’s volume fraction.

3.6. Micromechanical analysis using large scale hybrid Monte-Carlo FEA simulations

Existing micromechanical investigations of the effective mechanical properties of CNT-reinforced composites typically employ linear analytical formulations such as the Mori–Tanaka scheme presented above (Loos, 2013; Tsai et al., 2012; Abdellatif and Hedi, 2011). These investigations certainly assist in understanding the effects of such parameters as CNT concentration, aspect ratio, and orientation upon the linear elastic properties of the bulk composite. However, it is also of interest to the scientific community to understand how these parameters govern the full constitutive response of the nanocomposite subject to large deformations. Here, we must adopt an alternative approach utilizing traditional continuum FE concepts coupled with MC techniques to develop large scale three-dimensional micromechanical models that can be used to predict the resulting stress and strain fields in the nanocomposite for large deformations. Below we describe the development of such a model.

3.6.1. Representative fiber constitutive model

As in the linear-elastic micromechanical analysis using the Mori–Tanaka method presented above, a constitutive model for both the representative fiber and surrounding epoxy matrix that accounts for the material nonlinearities must be determined. The finite element platform offers a number of nonlinear material models that can be used to simulate a wide variety of materials. In our current simulations we employ multi-linear elastic material models to describe the nonlinear behavior of the nanocomposite constituents. Again, the RVE described in Section 2 provides the basis for determining such a constitutive law for the representative fiber which can be used to model the reinforcing phase. Recall that each of the constituent materials in the RVE is modeled using nonlinear formulations. This effectively allows for the full response of the RVE to be determined when subject to large deformations. As such, the RVE is loaded in tension by applying displacement boundary conditions to the nodes at the upper surface while constraining all degrees of freedom at the base of the RVE. The RVE is loaded to a maximum strain of 20%. Using the dimensions provided in Fig. 7 results in the RVE exhibiting a CNT volume fraction of 32% which will become an important parameter to consider when evaluating the true CNT concentration in the bulk nanocomposite. The constitutive response is then evaluated by summing the reaction forces of all the nodes on the upper surface of the RVE and dividing by the cross-sectional area during each iteration. This approach results in the following constitutive response depicted in Fig. 9 which exhibits a Young’s modulus of 460 GPa. This response is used as the constitutive law for the equivalent homogeneous representative fiber.
epoxy matrix, on the other hand, exhibits the constitutive response presented in Fig. 4.

3.6.2. Monte-Carlo computational cell

In order to simulate the bulk response of the CNT-reinforced epoxy nanocomposite, a three-dimensional computational cell representative of the material in question must first be developed. It is worth noting that while two-dimensional FE models could be geometrically acceptable for platelets, they cannot accurately describe the geometry for cylindrical and spherical inclusions (Sheng et al., 2004; Hbaieb et al., 2007). Hbaieb et al. (2007) has shown that in the case of randomly distributed cylindrical clay particles, 2D finite element models considerably underestimate the predictions of 3D models.

Here, we develop a Monte-Carlo based algorithm that randomly disperses the appropriate number of reinforcing representative fibers in the surrounding matrix. We impose periodic boundary conditions on the cell and ensure that no reinforcing representative fibers are in contact or overlap using an algorithm that calculates the shortest distance between two line segments in three-dimensions. The model only considers perfectly straight reinforcing representative fibers of diameter equal to that of the RVE, 2.4 nm, and aspect ratio of 100. The authors acknowledge that CNTs exhibit a degree of curvature and rarely remain straight particularly in random dispersion. However, the focus of the current work is to demonstrate the predictive and nonlinear capabilities of the proposed multiscale modeling approach for an idealized case. The model has the capabilities to be extended for the case of wavy reinforcing CNTs and will be the focus of future publications. The computational cell is a cube having equal dimensions along all sides. A key parameter that governs the accuracy of the results is the size of the computational cell. If too small a cell size is selected, the model will not be representative of the material and will ultimately suffer from boundary effects (Hbaieb et al., 2007). On the other hand, the computational complexity of the model scales heavily with computational cell size as well as CNT volume fraction and aspect ratio. This clearly demonstrates the need to identify an adequate cell size which is large enough to preserve the physics of the problem but small enough to avoid demanding computational costs. This also demonstrates the need for high powered computing resources (HPC) to conduct these simulations as it pushes the computational limits of standard university workstations. As such, these simulations are run using SharcNet’s HPC supercomputer resources. The main steps involved in developing these large-scale hybrid Monte-Carlo FEA models are summarized in Table 6 and schematically shown in Fig. 10.

Following the steps above will result in a computational cell with randomly dispersed representative fibers with periodic boundary conditions. The next important step is to mesh the model using HyperMesh’s highly adaptive meshing algorithm. Here, we use higher ordered 3-D, 10-node solid tetrahedral elements with quadratic displacement behavior to mesh both the polymer and representative fiber. The element is defined by 10 nodes having three degrees of freedom at each node: translations in the nodal x, y, and z directions. Fig. 11 depicts one such model prior to meshing of the surrounding adhesive and after. The model adopts a CNT aspect ratio of 100 and a representative fiber volume fraction of 1.56% which corresponds to a CNT concentration of 0.5 vol%.

4. Results and discussion

4.1. Effective linear elastic properties of nano-reinforced adhesives

In the following, we investigate the sensitivity of the effective linear elastic properties of nano-reinforced adhesives on the CNT volume fraction, orientation and aspect ratio, a. Here we adopt the Mori–Tanaka micromechanical modeling method as described in Section 3.5. The experimental program of this thesis only considers a randomly orientated dispersion of CNTs in the adhesive matrix. In fact, Fig. 12 shows an STEM micrograph of the nano-reinforced adhesives with a CNT concentration of 1.0 wt%. Clearly, the CNTs show no preferential alignment in the matrix. However, for the sake of completeness, we do present the variation of the elastic constants for nano-reinforced adhesives containing fully aligned CNTs.

The variation of the longitudinal Young’s modulus, $E_l$, and transverse Young’s modulus, $E_t$, of nano-reinforced adhesives containing aligned CNTs are plotted in Figs. 13 and 14, respectively. Both moduli exhibit similar trends, with increasing CNT volume fraction, both $E_l$ and $E_t$ increase significantly. At a CNT concentration of 10 vol% and an aspect ratio of 100 a 34 and 2.4-fold increase is observed in $E_l$ and $E_t$, respectively. In comparison, Lusti and Gusev (2004) observed an enhancement by a factor of 30–40 in $E_l$ for the fully aligned CNT case with comparable material properties in their micromechanical analysis. An increase in the CNT aspect ratio also results in a significant increase in both the longitudinal and transverse Young’s moduli at low values of $\alpha$. However, for aspect ratios above 200 relatively small increases are observed in $E_l$ and $E_t$ as shown in Figs. 15 and 16, respectively. Yu et al. (2011) reported a similar trend in their micromechanical analysis and observed a critical aspect ratio in the range of 100. The longitudinal shear modulus, $G_l$, and the transverse shear modulus, $G_t$, of nano-reinforced adhesives containing aligned CNTs are plotted against the CNT volume fraction in Figs. 17 and 18, respectively. It can be observed that both $G_l$ and $G_t$ exhibit a moderate increase with an increase in CNT concentration. However, both moduli show only a moderate initial decrease with increasing aspect ratio up to a value of 10 and remain constant for further increases of $\alpha$ indicative that the longitudinal and transverse shear moduli are insensitive to the CNT aspect ratio as shown in Figs. 19 and 20. It is difficult to explain the initial subtle decrease of both shear moduli at low CNT aspect ratios. However, these results seem to suggest that reinforcing phases that closely replicate the spherical geometry better influence the shear properties. Comparable trends were observed in the works of Odegard et al. (2003) which also indicate an insignificant dependency of the shear moduli on the CNT aspect ratio.

It should be noted that the CNT volume fraction has been extended up to a maximum of 5%. CNT concentrations above this magnitude are not normally realized. The attractive van der Waals interactions between CNTs coupled with their high aspect ratio leads to considerable agglomeration and aggregation at high CNT concentrations. The resulting agglomerates act as defect sites.

![Fig. 9. Constitutive response of RVE for the case of 32% CNT volume fraction.](image-url)
Table 6
Steps involved in the development of the computational cell.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Construct computational cell using specified dimensions (i.e. cell length = 65 nm)</td>
</tr>
<tr>
<td>2</td>
<td>Disperse representative fiber at a random location with its centroid located within the bounds of the computational cell</td>
</tr>
<tr>
<td>3</td>
<td>Check if representative fiber extends beyond the boundaries of the cell. If so then truncate the representative fiber and impose periodic boundary conditions</td>
</tr>
<tr>
<td>4</td>
<td>Check if new truncated segment of representative fiber extends beyond the boundaries of cell. If so then repeat periodic boundary conditions</td>
</tr>
<tr>
<td>5</td>
<td>Disperse next representative fiber at a random location with its centroid located within the bounds of the computational cell</td>
</tr>
<tr>
<td>6</td>
<td>Check if representative fiber extends beyond the boundaries of the cell. If so then truncate the representative fiber and impose periodic boundary conditions</td>
</tr>
<tr>
<td>7</td>
<td>Check if new truncated segment of representative fiber extends beyond the boundaries of cell. If so then repeat periodic boundary conditions</td>
</tr>
<tr>
<td>8</td>
<td>Check if newest representative fiber segments overlap or contact existing representative segments. If so then delete newest representative fiber segments</td>
</tr>
<tr>
<td>9</td>
<td>Repeat until required volume fraction of representative fibers has been achieved</td>
</tr>
</tbody>
</table>

Fig. 10. Schematic of the steps involved in the development of the computational cell model.

Fig. 11. Hybrid Monte-Carlo FEA computational cell model in its (a) unmeshed and (b) fully meshed form. The model utilizes a CNT volume fraction of 1.0% and a CNT aspect ratio of 100.
rather than reinforcements which would ultimately lead to a subsequent degradation of the nanocomposite properties. An efficient utilization of the nanotube properties in polymeric materials is therefore related to their homogenous dispersion in the matrix. The present study uses an idealized model which assumes a perfect dispersion of the nanophase particles even at these high concentrations. Therefore, we can expect that the results would indicate a positive influence of the nanotubes on the elastic properties even at higher CNT volume fractions.

in the inset. In that inset, we extend the results to a 100% CNT volume fraction to illustrate the unrealistic positive reinforcement effect at high CNT concentrations.

Figs. 21 and 22 show the effect of CNT volume fraction on the Young’s modulus, $E$, and shear modulus, $G$, of nano-reinforced adhesives containing randomly orientated CNTs, respectively. Both moduli exhibit an increase with increasing CNT volume fraction and aspect ratio. Furthermore, unlike the case for aligned CNTs, both moduli exhibit the common trend of an initial increase with increasing aspect ratio up to a value of approximately 200 as shown in Figs. 23 and 24. Figs. 25 and 26 compare Young’s
modulus and the shear modulus for nano-reinforced adhesives containing both aligned and randomly orientated CNTs for the case where $\alpha = 100$, respectively. As expected, the Young’s modulus for the aligned composite is significantly higher than the random case, however, the opposite is true for the shear modulus. At a CNT concentration of 5.0 vol% the Young’s modulus is enhanced by more than a factor of 5 while the shear modulus suffers by a factor greater than 6 through the alignment of the CNTs. This same trend was also observed in the Mori–Tanaka analysis of CNT polymer composites by Odegard et al. (2003).

4.2. Full constitutive response predictions

The Mori–Tanaka micromechanical modeling technique allowed for the prediction of the effective linear elastic properties nano-reinforced adhesives. These results are particularly helpful in understanding how the homogeneous dispersion of CNTs in the examined epoxy will influence the elastic properties for varied CNT concentrations, aspect ratios and orientations. However, it is also desirable to understand how the dispersion of CNTs will influence the full constitutive response of the nano-reinforced adhesive subject to mechanical loads. In the following we present an initial prediction of the full constitutive response of the bulk
nano-reinforced adhesive under large tensile deformations using the hybrid MC-FEA computational micromechanical model presented in Section 3.6. In view of the insensitivity of most elastic moduli to CNT aspect ratios above 200, as determined by the previous micromechanical analysis, and the scaling computational demand associated with modeling high aspect ratios, we adopt a CNT aspect ratio of 100 in the current analysis. We also note that CNTs exhibit a degree of curvature and rarely remain straight over their entire length as shown in the STEM micrograph of Fig. 27. Therefore, there is a decreased likelihood of a typical nanotube remaining straight as the nanotube length exceeds 100 nm. We also impose a condition of perfect bonding between the CNT and the surrounding matrix.

4.2.1. Cell convergence analysis

A key parameter that governs the accuracy of the results is the size of the computational cell. If too small a cell size is selected, the model will not be representative of the material and will ultimately suffer from boundary effects. On the other hand, the computational complexity of the model scales heavily with computational cell size as well as CNT volume fraction and aspect ratio (Gusev, 1997). This clearly demonstrates the need to identify an adequate cell size which is large enough to preserve the physics of the problem but small enough to avoid demanding computational costs. Therefore, a convergence analysis using the Young’s modulus of the nano-reinforced adhesives as the criterion was selected to study the effect of the computational cell size. Fig. 28 depicts several computational cell models in their final form. For all cases, the models assume a CNT aspect ratio of 100 and a representative fiber volume fraction of 1.6% which corresponds to a CNT concentration of 0.5 vol%. To maintain this concentration over the different cell sizes considered, additional CNTs are added to the models such that the cases of 4, 7, 14, 21, and 35 CNTs are considered.

The cell size convergence plot is depicted in Fig. 29. Also shown on the secondary vertical axis is the number of elements for each case. As can be seen, the Young’s modulus of the nano-reinforced adhesive initially increases with the number of CNTs considered and eventually begins to plateau near the case of 14 CNTs which only exhibits a 9% discrepancy from the case of 35 CNTs but at a fraction of 1/3 the total elements. Given this result, the cell size which incorporates 14 CNTs, or equivalently, has a cell length of 81.88 nm is used throughout the remainder of the analyses. Fig. 30 shows the predicted constitutive response of the nano-reinforced adhesives under tensile load for the different cell sizes considered plotted along with an experimental measurement for the same CNT concentration of 0.5 wt%.

To date, the author is unaware of any existing attempts to characterize the full constitutive response of a 3-dimensional composite containing randomly dispersed discrete CNTs. However, several authors have employed a similar approach in the investigation of the linear elastic moduli of generic composites which also requires an evaluation of an optimal computational cell size. Mortazavi et al. (2013) developed 3D finite element models of random two-phase composites to examine the elastic moduli and thermal conductivities for a range of inclusion geometries. They fail to comment on the cylindrical geometry but report an optimal cell size containing 30 inclusions for the spherical geometry for the material properties considered. Hbaieb et al. (2007) also reported 30
inclusions as the optimal value in their micromechanical investigation of the elastic moduli of nanocomposites containing clay platelets. Gustev reports a cell size incorporating at least 64 random spherical inclusions (Gusev, 1997) while only 16 for the case of randomly orientated and aligned cylindrical fibers (Gusev, 2001). Given the above variance, it is clear that the optimal cell size is a function of a number of geometrical and material parameters.

4.2.2. Constitutive response for Varied CNT concentrations

With the appropriate cell size in place, the model was extended to investigate the constitutive response of the nano-reinforced adhesives at higher CNT concentrations. The same modeling procedure was adopted and additional representative fibers were included to achieve the desired concentrations that span 0.0–3.0 vol% in increments of 0.5 vol%. Fig. 31 depicts the constitutive response for all the models while Figs. 32 and 33 plot Young’s modulus and the tensile strength over the concentrations considered, respectively. The constitutive responses show the same overall trend while Figs. 32 and 33 indicate an approximately linear trend over the concentrations considered. Each model adopts a random spatial and orientational distribution of CNTs. However, there is some degree of preferential alignment which can explain the minor deviations from linearity. Also shown in Fig. 32 is the result of the linear Mori–Tanaka method for randomly orientated CNTs for an aspect ratio of 100. Clearly, both the Mori–Tanaka predictions and those of the hybrid MC/FEA model are in close agreement. However, the hybrid result slightly underestimates the predictions of the Mori–Tanaka method. Again, we attribute this discrepancy to the preferential alignment effect and also the fact the Mori–Tanaka scheme uses an analytical averaging procedure that spans all possible CNT orientations.

One should note that the linear trend is rarely observed in an experimental setting. CNTs have the tendency to agglomerate at high concentrations and the agglomerates act as defect sites rather
than reinforcements. Fig. 34 shows a STEM micrograph of one such agglomerate embedded in a nano-reinforced adhesive for the case of 3.0 wt% CNT loading. There tends to be a critical CNT concentration above which the properties of the composite begin to degrade. In order to achieve this degradation in the predicted results the model must be extended to investigate the effect of CNT agglomeration and introduce additional parameters related to the size and density of the agglomerates. The current model is fully capable of such an extension. However, introducing the additional agglomerate dimension would require a much larger computational cell that can accommodate the new microstructure and preserve the physics of the problem.

5. Conclusions

A novel multiscale modeling technique that integrates governing atomic constitutive laws in a continuum framework is developed for the characterization of nano-reinforced composites. This technique takes into account the discrete nature of the atomic interactions at the nanometer length scale and the interfacial characteristics of the nanotube and the surrounding adhesive matrix. Appropriate formulations are developed to allow for the ABC modeling of nano-reinforced adhesives on the basis of a nanoscale RVE that accounts for the nonlinear behavior of its constituents. The RVE is in turn used with analytical and numerical micromechanical techniques to scale up to the macrolevel and to provide a prediction of the bulk effective mechanical properties. The analytical approach provides a means of predicting the linear elastic properties for aligned and randomly orientated CNTs. The numerical approach takes the form of a large scale 3D hybrid MC-FEA model that allows for the full prediction of the constitutive response of the nano-reinforced adhesives under large displacements. These multiscale solutions indicate a substantial reinforcement effect from the homogeneous dispersion of CNTs.

Acknowledgements

The authors wish to acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Qatar National Research Fund.

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