Interfacial and mechanical properties of epoxy nanocomposites using different multiscale modeling schemes

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A B S T R A C T
In this study, we investigate the interfacial and mechanical properties of carbon nanotube (CNT) reinforced epoxy composite. The work carried out in two stages. In the first, we conducted molecular dynamics (MD) simulations to determine the atomic-level interfacial and mechanical properties of the transversely isotropic representative volume element (RVE) comprised of CNT-epoxy composite. In the second, the Mori–Tanaka micromechanics scheme was used to scale up the mechanical properties of the atomic structure to the microscale level. The work was further extended and used atomistic-based continuum (ABC) multiscale modeling technique, which makes use of constitutive relations derived solely from interatomic potentials to model the same system. Interestingly, the results of our comparative investigation reveals that (i) the ABC technique and MD simulation provide almost identical predictions for the atomic-level interfacial and mechanical properties of the nanocomposite, (ii) both models predict comparable bulk mechanical properties of the nanocomposite containing randomly dispersed CNTs, and (iii) they also reveal that a higher degree of orthotropy of the nanoscale representative fiber significantly influences the bulk mechanical properties of the nanocomposite.

1. Introduction

The remarkable physical and thermomechanical properties of CNTs, such as low density [1], high aspect ratio [2], high Young’s modulus [3–6], high thermal conductivity [7–9], low coefficient of thermal expansion [10,11], high strength [12–14] and large fracture strain [13,14] have made them excellent reinforcements for multifunctional composites. It is found that few weight percentages of CNTs can significantly improve the interfacial and mechanical properties of CNT-based composites.

Several experimental studies have been carried out to investigate the interfacial characteristics of CNT-reinforced composites. For instance, Wagner et al. [15] estimated the interfacial shear stress between the multi-walled CNTs and the polymer based on the fragmentation test to be as high as 500 MPa, which is more than one order of magnitude compared with conventional composites. Micro-Raman spectroscopy was used by Ajayan et al. [16] to measure the local mechanical behavior of single-walled CNT bundles in an epoxy nanocomposite. They noticed that the efficiency of stress transfer and hence the enhancement of the mechanical properties is lower than expected due to sliding of the CNTs in the agglomerated bundles. Qian et al. [2] investigated the load transfer in multi-walled CNT-polystyrene composites and reported that addition of 1 wt% of CNTs increases the tensile modulus and strength by ~39% and 25%, respectively. Schadler et al. [17] studied the interfacial characteristics of multi-walled CNT-reinforced composites with both the tension and compression loadings. They reported that the compression modulus is higher than that of the tensile modulus, indicating that the load transfer to CNTs from the matrix is higher in compression. Cooper et al. [18] used scanning probe microscope tip to pull-out individual single- and multi-walled CNTs ropes from epoxy matrix. The ISS of both cases was found to be in the range of 35 to 376 MPa. This relatively high value of ISS was attributed to the formation of a strong ultrathin epoxy layer at the interface. This layer exits as a result of the formation of covalent bonds between CNTs and the surrounding polymer molecules, which originate from the presence of defects in the CNTs.

A significant number of analytical and numerical studies have also been conducted to investigate the interfacial properties of CNT-based composites. For example, Lordi and Yao [19] used force-field based molecular mechanics calculations to determine the binding energies and sliding frictional stresses between CNTs and a range of polymer substrates, in an effort to understand the factors governing interfacial strength. They reported that binding...
energies and frictional forces play only a minor role in determining the strength of the interface, but that helical polymer conformations around the CNT are essential in developing high ISS. Liao and Li [20] studied the interfacial characteristics of a CNT-reinforced polystyrene composite system through molecular mechanics simulations and elasticity calculations. They reported that the CNT-matrix bonding arises from non-bonded electrostatic and van der Waals (vdW) interactions, deformation induced by these interactions, and mismatch in the coefficients of thermal expansion. Their CNT pull-out simulation results suggest that the interfacial shear stress of the CNT-polystyrene system is about 160 MPa; significantly higher than conventional carbon fiber composite systems. Frankland et al. [21] generated stress-strain curves of polyethylene nanocomposite reinforced with long and short CNTs using MD simulations. Both nanocomposites were mechanically loaded in the axial and the transverse directions of the CNT axis. In their study, nanocomposite reinforced with long CNTs showed an increase in the stiffness relative to the polymer. On the other hand, nanocomposites reinforced with short CNTs showed no enhancement relative to the polymer. Xiao and Zhang [22] studied the effects of CNT length and diameter on the distributions of the tensile stress and interfacial shear stress of a CNT in an epoxy matrix. Their work revealed that a smaller CNT diameter has a more effective reinforcement effect than a solid fiber, and provides toughness and tensile strength to the reported that a CNT has a greater stress transfer efficiency than a mal tube length at which reinforcement is maximized. They also showed a more effective reinforcement effect and that there exists an opti-

epoxy matrix. Their work revealed that a smaller CNT diameter has been developed by Li and Saigal [24] for assessing the interfacial and mechanical properties of CNT-reinforced polymer composite materials. An expression for the effective length of the CNT has also been established by them for studying the load transfer efficiency in CNT-reinforced composites. A micromechanics model has also been developed by Haque and Ramasetty [23] to study the axial stress and shear stress at the interface of CNT-reinforced polymer composite materials. Evidently, a number of experimental, analytical and numerical works has been reported in the literature to investigate the interfacial and mechanical properties of CNT-based composites. Among all these, we consider the multiscale modeling technique is more appropriate to property evaluation of CNT-based compos-

ties. It is, therefore, our objective to develop a multiscale model capable of characterizing both the interfacial and mechanical properties of CNT-reinforced epoxy composite. This task was performed in two steps. In the first, MD simulations were used to study the interfacial and the transversely isotropic mechanical properties of the nanoscale RVE containing CNT embedded in epoxy. In the sec-

ond, the determined mechanical properties of the nanoscale RVE were used to determine the bulk mechanical properties of the nanocomposite using Mori–Tanaka model. Fig. 1 demonstrates the steps involved in the hierarchical multiscale model. To our knowledge, among the reported multiscale models, a newly devel-

oped atomistic based continuum model known here after as ABC [38,41,46] is the first which has successfully described the atomic-property relations of CNT-reinforced polymer composite in a continuum framework. In comparison to other multiscale models, ABC technique distinguished its novelty by incorporating the nanoscale transversely isotropic RVEs in determining interfa-

cial and mechanical. In fact, Meguid and coworkers [38,41,46] reported both the interfacial and mechanical properties of CNT-reinforced polymer composites using ABC technique and suc-
ceded in investigating the influence of different parameters, such as embedded CNT length, thickness of the CNT-polymer interface, CNT diameter and LJ cut-off distance. In view of this, our MD-Micromechanics based multiscale modeling approach was compared with this novel ABC approach. For the sake of complete-

ness, we provide below a summary of the two approaches used in modeling the current CNT-Composite system.

2.1. Molecular dynamics modeling and simulations

This Section is devoted fully to molecular dynamics modeling and simulations. All MD runs were conducted with the aid of large-scale atomic/molecular massively parallel simulator

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![Image](https://via.placeholder.com/150)

**Fig. 1.** Modelling steps involved in the developed multiscale model.
(LAMMPS) [47] by using the consistent valence force field (CVFF) [48]. Conjugate gradient algorithm was used to minimize the total potential energy of the initial configurations, while velocity Verlet algorithm was used to integrate the equations of motion in all MD simulations. Periodic boundary conditions were imposed on all directions of the MD unit cells. In the simulations, the non-bonded interactions between the atoms are represented by vdW interactions and Coulombic forces. Determination of the atomic-level mechanical properties of the pure epoxy and the nanocomposite RVE was accomplished by straining the MD unit cells followed by constant-strain energy minimization. The average value of the stress tensor of the MD unit cell is defined in the form of virial stress [43]; as follows

$$\sigma = \frac{1}{V} \sum_{i=1}^{N} \left( \frac{m_i}{2} \ddot{r}_i + F_i \right)$$

where $V$ is the volume of the RVE; $\dot{r}_i$, $m_i$, $r_i$, and $F_i$ are the velocity, mass, position and force acting on the $i^{th}$ atom, respectively.

2.1.1. Modeling of pure epoxy

To model the matrix, we used a specific two-component epoxy material based on a diglycidyl ether of bisphenol A (DGEBA) epoxy resin and triethylene tetramine (TETA) curing agent, which is typically used in aerospace industry. During the curing process, the hydrogen atoms in the amine groups of the hardener (TETA) react with the epoxide groups of the resin (DGEBA) forming covalent bonds, which result in a highly cross-linked epoxy structure [49]. The resin/curing agent weight ratio in the epoxy polymer was set to 100:16.7. The epoxy system was generated by packing the MD unit cell with epoxy oligomers [50]. Every epoxy oligomer consists of six DGEBA molecules connected by one TETA molecule, as shown in Fig. 2. The main steps involved in determining the elastic moduli of pure epoxy are as follows:

**Step 1 (Minimization):** The initial epoxy configuration was optimized to its minimum energy configuration using the conjugate gradient algorithm. The system is considered to be optimized once the change in the total potential energy of the system between subsequent steps is less than $1.0 \times 10^{-10}$ kcal/mol.

**Step 2 (Equilibration):** The amorphous structure obtained from the minimization step was then equilibrated at room temperature in the constant temperature and volume canonical (NVT) ensemble. The equilibration process is carried out over 25 ps by using a time step of 0.5 fs. The system was then equilibrated for another 25 ps in the isothermal–isobaric (NPT) ensemble at 300 K and 1 atm to generate a compressed structure with the correct density and residual stresses. This equilibration step resulted in an equilibrated amorphous structure with an average density of 1.09 g/cm$^3$. At the end, the structure is again equilibrated for 25 ps in the NVT ensemble at 300 K to obtain an equilibrated structure with minimum energy.

**Step 3 (Uniaxial tension):** Uniaxial tensile test is carried out to determine the elastic moduli of the epoxy material. Constant uniaxial strain increments of 0.25% were applied along particular direction by uniformly expanding the unit cell along this direction and updating the atoms coordinates to fit within the new dimensions. After each strain increment, the MD unit cell is equilibrated using the NVT ensemble at 300 K for 5 ps. Then, the stress tensor is averaged over an interval of 5 ps to reduce the effect of fluctuations. These steps were repeated again in the subsequent deformation increments. The procedure was stopped when the total strain reached 2.5%. The same simulation steps were adopted to determine the stress–strain curves for the other two directions and then the recorded stress–strain data were averaged over all directions.

The initial molecular configurations of an amorphous epoxy are constructed by randomly placing 45 epoxy oligomers inside an MD cell of size $60 \times 60 \times 60$ Å using Packmol software [50]. The details of pure epoxy RVE are summarized in Table 1. The total number of atoms in this cubic cell is 25354, which represent an ensemble. The equilibration process is carried out over 25 ps by using a time step of 0.5 fs. The system was then equilibrated for another 25 ps in the isothermal–isobaric (NPT) ensemble at 300 K and 1 atm to generate a compressed structure with the correct density and residual stresses. This equilibration step resulted in an equilibrated amorphous structure with an average density of 1.09 g/cm$^3$. At the end, the structure is again equilibrated for 25 ps in the NVT ensemble at 300 K to obtain an equilibrated structure with minimum energy.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pure epoxy</th>
<th>RVE to determine RDF</th>
<th>Nanocomposite RVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT type</td>
<td>–</td>
<td>(9, 9)</td>
<td>(9, 9)</td>
</tr>
<tr>
<td>CNT diameter (Å)</td>
<td>–</td>
<td>12.2</td>
<td>12.2</td>
</tr>
<tr>
<td>CNT length (Å)</td>
<td>–</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>RVE dimensions (Å$^3$)</td>
<td>$60 \times 60 \times 60$</td>
<td>$50 \times 50 \times 43$</td>
<td>$31 \times 31 \times 43$</td>
</tr>
<tr>
<td>CNT volume fraction</td>
<td>–</td>
<td>5.5%</td>
<td>12.16%</td>
</tr>
<tr>
<td>Total number of atoms</td>
<td>25354</td>
<td>12690</td>
<td>4340</td>
</tr>
</tbody>
</table>

Fig. 2. Chemical structures of (a) epoxy resin (DGEBA), (b) curing agent (TETA), and (c) cured epoxy oligomer consists of 6 DGEBA molecules connected by single TETA molecule.
epoxy system with an average density of 1.09 g/cm³. The average elastic constants of the epoxy were calculated from the slope of the stress–strain curves generated from the uniaxial tensile loadings. Young’s modulus and Poisson’s ratio of pure epoxy are determined to be 1.2 GPa and 0.35, respectively.

2.1.2. CNT-epoxy interface layer thickness

The structure of the epoxy matrix at the vicinity of the CNT surface differs from the bulk epoxy due to the formation of an ultra-thin epoxy layer at the CNT-epoxy interface. This ultra-thin layer at the CNT-epoxy interface, which is ignored by many researchers, consists of a highly packed crystalline polymer, which has higher elastic properties than the amorphous bulk polymer [18,28]. In order to obtain the actual CNT-epoxy properties, the size of the RVE must be large enough to incorporate the change of the polymer structure. The cylindrical molecular structure of the CNT is treated as an equivalent solid cylindrical fiber [29–31,33,34,36] for determining its volume fraction in the nanocomposite RVE.

\[
\text{CNT volume fraction} = \frac{L_{\text{CNT}} \times \frac{\pi}{4} (d_{\text{CNT}}^2 + h_{\text{vdW}}^2) - (d_{\text{CNT}} - t_{\text{CNT}})^2}{V}
\]

where \(d_{\text{CNT}}, L_{\text{CNT}}\) and \(t_{\text{CNT}}\) denote the respective diameter, length and thickness of a CNT, and \(h_{\text{vdW}}\) is vdW equilibrium distance between the CNT and the surrounding polymer matrix.

To determine the thickness of the interface layer, we performed a MD simulation for a system consisting of a CNT of length 43.0 Å surrounded by 51 epoxy oligomers. The size of the periodic RVE was \(50 \times 50 \times 43\) Å and its details are summarized in Table 1. Subsequently, the RVE is equilibrated using the same modeling steps as described above for pure epoxy. Fig. 3 shows the radial distribution function (RDF) of the epoxy atoms that surround the CNT after the equilibration. The variation of the RDF along the radial direction represents the change of the epoxy structure in the vicinity of the embedded CNT. It may be observed from Fig. 3 that the RDF of epoxy atoms is zero at the radial distance of 8 Å and reaches its maximum value of 360 atoms/nm³ at the radial distance of 9.5 Å. Then, it starts to fluctuate around an average value of 225 atoms/nm³. Fig. 4 shows a close view of the equilibrated
RVE. The obtained values of the interface thickness and the equilibrium separation distance were used in Section 4.1 to select the appropriate RVE size.

2.1.3. CNT pull-out simulations

Amongst the most common approaches for measuring the ISS of the CNT-polymer nanocomposite is the pull-out test. During the pull-out simulations, one-end of the fully embedded CNT is extracted from the matrix at constant pull-out rate or velocity of $1 \times 10^{-5}$ Å/fs in the NVT ensemble at 300 K [51]. The periodic boundary conditions were removed along the axial direction of the CNT and the matrix was constrained during the pull-out simulation [52]. The pull-out force and the average ISS were then determined based on the work done during the pull-out test. Typical snapshots during CNT pull-out from epoxy matrix are depicted in Fig. 5.

2.2. Effective mechanical properties of nanocomposite

MD simulations were then used as the basic unit to allow the determination of the effective mechanical properties of the resulting nanocomposite using micromechanics. It is well known fact that CNT-reinforced composite behaves anisotropically when subjected to the different loading conditions [21,34,41,44]. Therefore, the RVE was assumed to be transversely isotropic with the 1-axis being the axis of symmetry. To determine its five elastic constants, the RVE is subjected to five different tests: longitudinal tension, transverse tension, in-plane tension, in-plane shear and out-of-plane shear. The steps involved in the MD simulations for obtaining the elastic coefficients of the RVE are the same as adopted in the case of pure epoxy. Finally, a set of loading conditions were applied to the RVE, to determine the corresponding five independent elastic coefficients of the RVE, as listed in Table 2.

The elastic moduli of the pure epoxy and the nanocomposite RVE obtained from the MD simulations are used as inputs to the micromechanical model in order to determine the bulk mechanical properties of the nanocomposite. With this process firmly established in several studies [38–41], the Mori–Tanaka model [53,54] can be developed by utilizing the transversely isotropic elastic properties of the nanocomposite RVE and the isotropic properties of the pure epoxy matrix. In case of two-phase composite, where the inhomogeneity is randomly oriented in the three-dimensional space, the following relation can be used to determine the effective stiffness tensor [C] of the nanocomposite:

$$[C] = [C^m] + v_{RVE}([C^{RVE}] - [C^m])[A][v_m][I] + v_{RVE}([A])^{-1}$$  \hspace{1cm} (3)

in which the mechanical strain concentration tensor [A] is given by

$$[A] = [I] + [S^{RVE}](C^m)^{-1} ([C^{RVE}] - [C^m])^{-1}$$  \hspace{1cm} (4)

where $[C^m]$ and $[C^{RVE}]$ are the stiffness tensors of the epoxy matrix and the RVE, respectively; $[I]$ is an identity matrix; $v_m$ and $v_{RVE}$ represent the volume fractions of the epoxy matrix and the RVE, respectively; and $[S^{RVE}]$ indicate the Eshelby tensor. The specific form of the Eshelby tensor for the RVE inclusion given by Qiu and Weng [55] is utilized herein.

It may be noted that the elastic coefficient matrix [C] directly provides the values of the effective elastic properties of the nanocomposite, where the RVE is aligned with the 1-axis. In case of random orientations of CNTs, the terms enclosed with angle brackets in Eq. (3) represent the average value of the term over all orientations defined by transformation from the local coordinate system of the RVE to the global coordinate system. The transformed mechanical strain concentration tensor for the RVEs with respect to the global coordinates is given by

$$\tilde{[A]}_{ijkl} = t_{ip}t_{jq}t_{kr}[A]_{rs}$$  \hspace{1cm} (5)

where $t_{ij}$ are the direction cosines for the transformation and are given by

$$t_{11} = \cos \phi \cos \psi - \sin \phi \cos \gamma \sin \psi, \quad t_{12} = \sin \phi \cos \psi + \cos \phi \cos \gamma \sin \psi, \quad t_{13} = \sin \psi \sin \gamma,$$

$$t_{21} = -\cos \phi \sin \psi - \sin \phi \cos \gamma \cos \psi, \quad t_{22} = -\sin \phi \sin \psi + \cos \phi \cos \gamma \cos \psi, \quad t_{23} = -\cos \psi \sin \gamma,$$

$$t_{31} = \sin \phi \sin \gamma, \quad t_{32} = -\cos \phi \sin \gamma \cos \psi, \quad t_{33} = \cos \gamma$$

Consequently, the random orientation average of the mechanical strain concentration tensor $[A]_r$ can be determined by using the following equation [56]:

$$[A]_r = \frac{\int_{\phi=0}^{\pi} \int_{\psi=0}^{\pi/2} \int_{\gamma=0}^{\pi} [A](\phi, \psi, \gamma) \sin \gamma d\phi d\psi}{\int_{\phi=0}^{\pi} \int_{\psi=0}^{\pi/2} \int_{\gamma=0}^{\pi} \sin \gamma d\phi d\psi}$$  \hspace{1cm} (6)

where $\phi, \gamma, \psi$ are the Euler angles in degrees defined with respect to three successive rotations about the principal X, Y and Z coordinates. It may be noted that the averaged mechanical strain concentration tensors given by Eqs. (4) and (6) are used for the cases of aligned and random orientations of CNTs, respectively, in Eq. (3).

3. Atomistic-based continuum (ABC) modeling

Recently, Meguid and coworkers [41,46] presented novel ABC modeling schemes to investigate the interfacial and mechanical properties of CNT-reinforced polymer composites. In their works, the problem is formulated by using a RVE which consists of the reinforcing CNT, the surrounding polymer matrix, and the
CNT/polymer interface as demonstrated in Fig. 6. The idea behind the ABC technique is to incorporate atomistic interatomic potentials into a continuum framework. In this way, the interatomic potentials introduced in the model to capture the underlying atomistic behavior of the different phases considered. Thus, the influence of the nanophase is taken into account via appropriate atomistic constitutive formulations. For the sake of completeness, we provide a brief outline of this technique detailed in their work [41,46].

Fundamental to their proposed concept is the notion that a CNT is a geometrical space-frame-like structure and the primary bonds between two nearest-neighbor atoms act like load-bearing beam members. 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. They adopted 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 their study are the same as those adopted by Belytschko et al. [57]. The Modified Morse potential is given by:

\[
E = E_b + E_s
\]

\[
E_b = D_b \left[ \left( 1 - \exp^{-\beta(r-r_0)} \right)^2 - 1 \right]
\]

\[
E_s = \frac{1}{2} k_b \left( \theta - \theta_0 \right)^2 \left[ 1 + k_{\text{ext}} \left( \theta - \theta_0 \right)^4 \right]
\]

where \( r_0 \) is the initial bond length, \( \theta_0 \) is the initial angle between adjacent bonds, \( D_b \) is the dissociation energy, \( \beta \) is a constant which controls the 'width' of the potential, and \( k_b \) and \( k_{\text{ext}} \) are the angle bending force constants.

Nonlinear rotational spring elements were used to account for the angle-bending component, while beam elements were used to represent the stretching component of the potential. To describe the behavior of the beam and rotational spring elements, they first derived material models for each which accurately represents the characteristics of the modified Morse potential. First, by deriving the stretching potential \( (E_b) \) with respect to the change in bond length and by utilizing the relationship, \( \varepsilon = (r - r_0)/r \), the following equation is obtained:

\[
F = 2\mu D_b \left( 1 - \exp^{-\beta \varepsilon} \right) \exp^{-\beta \varepsilon}
\]

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 \( (E_s) \) with respect to the change in rotation, the following expression is derived:

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

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 \( U \) interatomic potential is used to describe the vdW interactions at the CNT/polymer interface. The \( U \) potential is defined as

\[
U_{ij} = 4\mu \left[ \left( \frac{\psi}{\tau} \right)^{12} - \left( \frac{\psi}{\tau} \right)^{6} \right]
\]

where \( \mu \) is the potential well depth, \( \psi \) is the hard sphere radius of the atom or the distance at which \( E_b \) is zero, and \( r \) is the distance between the two atoms. In their study, the non-bonded interactions between the carbon atoms in the CNT and the atoms in the polymer were considered.

They adopted 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. The \( U \) parameters for the interactions considered in their work are summarized in Table 3. Again, by differentiating the potential with respect to the separation distance, the following expression for the vdW force between two interacting atoms is obtained:

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

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.

To model the surrounding epoxy matrix, a specific two–component epoxy is used based on a diglycidyl ether of bisphenol A (DGEBA) and triethylene tetramine (TETA) formulation. The Young’s modulus and Poisson’s ratio of the epoxy matrix was taken to be 1.07 GPa and 0.28, respectively. The epoxy was modeled by using higher ordered 3-D, 10-node solid tetrahedral elements with quadratic displacement behavior.

3.1. CNT pull-out

Fig. 7 shows a schematic of the displacement boundary conditions of the pull-out process. The nodes in the CNT are constrained

![Fig. 7. Polymer representation and pull-out boundary conditions [46].](image)
from any radial displacements and an incremental axial displacement boundary condition is applied to the top CNT nodes to initiate the pull-out process. The force required to withdraw the CNT from the matrix is evaluated over the course of the pull-out process by summing the reaction forces at the upper CNT nodes. The corresponding ISS was determined by dividing the maximum pull-out force by the initial interfacial area, \( A = \pi dl \), where \( d \) and \( l \) are the diameter and length of the embedded CNT, respectively.

3.2. Effective mechanical properties of nanocomposite

Appropriate ABC formulations were developed by Wernik and Meguid [41] to determine the elastic properties of the transversely isotropic nanoscale RVE comprised: the reinforcing CNT, the surrounding matrix and their interface. In order to scale-up to the macro level, the RVE was homogenized into a representative fiber exhibiting the same geometrical and mechanical characteristics in such way that it behaves as an equivalent continuous medium. The geometry of the linear-elastic, homogenous representative fiber is assumed to be cylindrical, similar to that of the RVE. Transversely isotropic elastic properties of the representative fiber were determined by equating the total strain energies of the RVE and representative fiber under identical sets of loading conditions as listed in Table 2. Subsequently, the developed representative fiber is then used with analytical and computational micromechanical modeling techniques to determine the bulk mechanical properties of the nanocomposite for varied CNT concentrations and aspect ratios.

4. Results and discussion

In this Section, we determine the interfacial and mechanical properties of the nanocomposite, and compare the same with those predicted by the ABC multiscale model.

4.1. Interfacial properties of nanocomposite

A series of MD simulations were carried out to determine the ISS of the nanoscale RVE reinforced with an individual CNT. The effects of such parameters as embedded CNT length, the thickness of the CNT-polymer interface, \( \mu \) cut-off distance and CNT diameter on the ISS are investigated and discussed. To investigate the effect of the pertinent parameters on the ISS, the same CNT type and its volume fraction in the RVE are considered as considered by Wernik et al. [46].

4.1.1. Effect of embedded CNT length

Five different CNT lengths were considered to compare the MD results with those of the ABC results. It is well known that a short length of CNT significantly influences the interfacial characteristics of the resulting nanocomposite. Therefore, to reduce the computational effort, the maximum embedded CNT length in the polymer matrix is kept limited to 200 Å. Fig. 8 shows the effect of embedded CNT lengths on the ISS of a nanocomposite with an interfacial thickness of 3.4 Å. The ISS of the CNT-polymer composite system exhibits a decaying length trend similar to traditional fiber composites. It may also be observed that the ABC model slightly under predicts the ISS values. The subsequent MD simulations were carried out considering the embedded CNT length as being 200 Å.

4.1.2. Effect of CNT-polymer interfacial thickness

In existing studies, the CNT-polymer interfacial thickness has not yet been unambiguously defined. Several different values have been used in both atomistic and continuum simulations. For instance, Hu et al. [58] simulated the helical wrapping of one polystyrene chain around a CNT considering only vdw interactions using MD simulations. The equilibrium distance between the hydrogen atoms in the polymer and carbon atoms in the CNT ranged from 2.851 Å to 5.445 Å. However, only one polymer chain was considered, while in practical cases there may be other chains which also wrap around the CNT. Montazeri and Naghdabadi [59] used an interfacial thickness of 3.816 Å in their molecular structural mechanics model of CNT-reinforced polymer composites. This value corresponds to the equilibrium distance of the \( \mu \) potential. Hence, it is worthwhile to investigate the effect of different interfacial thicknesses on the ISS of CNT-reinforced polymer composite. Fig. 9 shows the predicted ISS for the nanocomposite system for an interfacial thickness range of 2.2–4.25 Å. This figure demonstrates that the ISS of the CNT-polymer composite system decreases with the increase in the interfacial thickness. This

\[
\text{ISS} = \frac{F_{\text{pull-out}}}{A}
\]

where \( F_{\text{pull-out}} \) is the pull-out force, \( A \) is the interfacial area.

<table>
<thead>
<tr>
<th>( \mu ) interaction</th>
<th>( \mu ) (J)</th>
<th>( \psi ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>( 10.285 \times 10^{-22} )</td>
<td>3.617</td>
</tr>
<tr>
<td>C–H</td>
<td>( 5.213 \times 10^{-22} )</td>
<td>2.45</td>
</tr>
<tr>
<td>C–O</td>
<td>( 12.767 \times 10^{-22} )</td>
<td>2.859</td>
</tr>
<tr>
<td>C–N</td>
<td>( 11.607 \times 10^{-22} )</td>
<td>3.501</td>
</tr>
</tbody>
</table>
phenomenon is attributed to the fact that vdW interactions between the CNT and the epoxy become weaker with the increase in their atomic separation distance. The trend of this finding is also well confirmed by the ABC technique. In the ABC study, as the interfacial thickness is decreased, a larger number of polymer atoms were included in the computational cell which increases the number of vdW interactions occurring over the interface and the subsequent ISS. Comparative trends also suggest that MD approach slightly overestimates the values of ISS over the ABC technique for the higher interfacial thicknesses. The subsequent MD simulations were carried out considering the CNT-polymer interfacial thickness as being 2.2 Å.

4.1.3. Effect of LJ cut-off distance

In most existing MD studies, the LJ interatomic potential used to simulate vdW interactions is often truncated to reduce the computational cost in such way that atom pairs whose distances are greater than the cut-off distance have zero vdW interaction energy. The cut-off distance is often taken to be 8.5 Å (see Ref. [46] and references therein). Truncating the potential introduces a sharp discontinuity between atoms inside and atoms outside the cut-off radius, particularly when smaller cut-off distances are used. Therefore, here an attempt is made to investigate the effect of LJ cut-off distance on the ISS of a nanocomposite. The LJ interatomic potential is defined in Eq. (12). The corresponding LJ parameters are listed in Table 4. Fig. 10 shows the estimated MD results for a cut-off range of 6 Å to 13 Å. As expected, the values of ISS of a nanocomposite system increase with the LJ cut-off distance and become stabilized at higher cut-off distance (> 12 Å). It may also be observed from Fig. 10 that both techniques predict the good agreement between the results for a wide range of cut-off distance.

4.1.4. Effect of CNT diameter

CNT diameter has a significant influence on the interfacial properties of the resulting nanocomposite. In this study, armchair CNT configurations are considered, with the smallest being a (5, 5) CNT, and the largest an (18, 18) CNT. Fig. 11 demonstrates that the predicted ISS decreases approximately linearly with the increase in the value of the CNT diameter. This finding demonstrates the advantage of using smaller diameter of armchair CNTs. Again, both multiscale modeling techniques (MD and ABC) show good agreement between the results for a wide range of CNT diameters. The marginal differences occur because an identical polymer configuration considered in the ABC study for all simulations in order to minimize the effect of polymer distribution on the pull-out curves.

4.2. Mechanical properties of nanocomposites

A series of MD simulations were carried out to determine the elastic properties of the transversely isotropic RVE reinforced with armchair (9, 9) CNT. The details of the RVE are summarized in Table 1. In our MD simulations, we made sure that the density of the epoxy matrix was set to 1.09 g/cm³, which is the same as that of the pure epoxy. Subsequently, a set of loading conditions were applied to the RVE to determine the corresponding five independent elastic coefficients of the RVE, as listed in Table 2. Table 5 summarizes the outcome of the MD simulations. It may be

<table>
<thead>
<tr>
<th>RVE</th>
<th>CNT volume fraction</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{22}$ (GPa)</th>
<th>$C_{13}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$C_{66}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present results</td>
<td>12.16%</td>
<td>116.4</td>
<td>6</td>
<td>7.5</td>
<td>15.1</td>
<td>3.8</td>
<td>2</td>
</tr>
</tbody>
</table>
observed from the results that the elastic properties of the RVE are significantly higher than those of the neat epoxy. In the next step of multiscale model, nanocomposite RVE will be used as an effective fiber in the Mori–Tanaka model to determine the bulk mechanical properties of the nanocomposite at the microscale level (see Fig. 1).

Considering the epoxy as the matrix phase and the transversely isotropic nanoscale RVE as the reinforcement, the bulk mechanical properties of the nanocomposite were determined by following the micromechanical modeling approach developed in Section 2.2. Practically, the orientations of the CNT reinforcements in the polymer matrix can vary over the volume of the nanocomposite. Therefore, studying the properties of nanocomposites reinforced with randomly oriented CNTs is of great importance. For such investigation, nanoscale RVEs are considered to be completely randomly dispersed in the epoxy matrix over the volume of the nanocomposite. The present multiscale model results are compared with those predicted by Wernik and Meguid [41] for CNT-reinforced composites containing randomly oriented transversely isotropic representative fibers. It may be noted that both models consider the maximum CNT volume fraction in the nanocomposite up to 5%. As expected, the randomly dispersed case provides the isotropic elastic properties for the resulting nanocomposite. Figs. 12 and 13 illustrate the variations of the bulk Young's and shear moduli of the nanocomposite with the CNT loading, respectively. The results predicted by both the multiscale models are in good agreement for the lower CNT loadings. The marginal difference between the results at the higher CNT loadings are attributed to the fact that the equilibrium distance between the carbon atoms of a CNT and the atoms of the polymer matrix is assumed as 3.8 Å in Ref. [41], while in the present study it is considered as 2.2 Å. In addition, a uniform distribution of the polymer nodal density (99 nodes/nm$^3$) around the embedded CNT is assumed in Ref. [41], while the polymer nodal density obtained from the MD simulations is found to vary along the radial direction, as shown in Fig. 3.

New fabrication techniques utilizing CNT fibers and arrays have emerged as means of producing nanocomposites with aligned CNT reinforcements [60]. Hence, the estimation of the bulk mechanical properties of the nanocomposite containing aligned RVEs along the 1–axis would be an important study. Therefore, the work was further extended to determine the bulk mechanical properties of the nanocomposite. The present multiscale model results are also compared with those predicted by Wernik and Meguid [41] for CNT-reinforced composites containing aligned representative fibers. For the comparison purpose, we considered their case of

![Fig. 13. Comparison of the bulk shear modulus of the nanocomposite containing randomly oriented CNTs.](image)

![Fig. 14. Comparison of the bulk (a) longitudinal Young's ($E_L$), (b) transverse Young's ($E_T$), (c) longitudinal shear ($G_L$), and (d) transverse shear ($G_T$) moduli of the nanocomposite predicted by the present multiscale model with those predicted by the ABC model.](image)
long CNTs embedded in the epoxy matrix having aspect ratio of 1000. Fig. 14 shows the variations of the elastic moduli of the nanocomposite against the CNT volume fraction. All moduli exhibit similar trends; with increasing CNT volume fraction, all moduli increase approximately linearly. It may be observed from Fig. 14(a) and (b) that the ABC multiscale model significantly over predicts the effective values of $E_t$ and $E_l$ over those of the present multiscale model. This phenomenon is mainly attributed to the effect of the degree of orthotropy of the nanoscale effective fibers (i.e., RVE and representative fiber) on the resulting nanocomposite. On the other hand, the present multiscale model slightly over predicts the effective values of $G_t$ and $G_l$ over those estimated by the ABC model. At this juncture it is important to mention that the effective transverse Young’s modulus of composite is matrix dominant. In contrast to this, the ABC model significantly over estimates the values of $E_t$. Therefore, the present multiscale model is considered to be an appropriate technique on the conservative side to determine the bulk elastic properties of the nanocomposite containing either randomly or aligned dispersed CNTs. In addition, it is important to note that the present multiscale model represents the real nanocomposite structure with the minimum assumptions compared to that of the ABC model which model the atomic structure as an equivalent beam and truss elements. Thus, it can be inferred from these comparisons that the present multiscale model can be reliably applied to determine the interface and mechanical properties of nanocomposites.

5. Conclusions

In this article, we developed a multiscale model to determine the interfacial and bulk mechanical properties of CNT-reinforced epoxy composites. Two aspects of the work were examined. First, MD simulations were carried out to determine the interfacial and the transversely isotropic elastic properties of the resulting nanoscale RVEs. Second, the developed RVEs were, in turn, used with analytical micromechanical technique of the Mori–Tanaka type to determine the bulk elastic properties of the nanocomposite. Furthermore, we carried out a detailed comparison between the MD and ABC predictions considering pertinent parameters, such as embedded CNT length, thickness of the CNT-polymer interface, CNT diameter, $L_j$ cut-off distance and orientations of dispersed CNTs. The following is a summary of our findings:

1. ISS results predicted by the MD and ABC techniques agree well with each other for a wide range of structural and geometrical parameters.
2. Both multiscale approaches indicate that the increase in a length of a CNT leads to a decrease in the values of ISS of the resulting nanocomposite.
3. They also indicate that the values of ISS of a nanocomposite system increase with the $L_j$ cut-off distance and become stabilized at higher cut-off value.
4. The bulk elastic properties of the nanocomposite containing randomly dispersed CNTs predicted by these techniques agree with each other.
5. The ABC model over predicts the longitudinal and transverse Young’s moduli of the nanocomposite containing aligned CNTs.

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References


