Multiscale Modeling of Nano-Reinforced Aerospace Adhesives

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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In this work, the mechanical properties of carbon nanotube reinforced structural adhesives are investigated both theoretically and experimentally. The theoretical investigations employ a novel multiscale modeling technique that integrates the governing atomistic constitutive laws in a continuum framework. 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 polymer matrix. Fundamental to the proposed concept is the notion that atomic bonds between two atoms act like load-bearing continuum elements, whereas individual atoms can be represented by nodes of the related structure. Molecular dynamic interatomic potentials were used to derive the constitutive behavior of the finite elements thereby reducing the computational complexity of the problem while maintaining the accuracy of the model. The governing formulations were developed to allow for the atomistic-based continuum modelling of nano-reinforced structural adhesive bonds on the basis of a nanoscale representative volume element that accounts for the nonlinear behaviour of its constituents; namely, the reinforcing carbon nanotube, the surrounding adhesive and their interface. This model was used to evaluate the constitutive response of carbon nanotubes with varied chiral indices, the load transfer and the strengthening mechanisms between the nanotube and the surrounding adhesive as well as their interfacial properties. The newly developed representative volume element was then used in
analytical (Mori-Tanaka) and computational (finite element) micromechanical modeling techniques to investigate the homogeneous dispersion of the reinforcing element into the adhesive considered upon its mechanical properties. In this way, the model allowed for the prediction of the full constitutive response of the bulk composite. The work is further extended experimentally to establish the relative merits of using carbon nanotubes as mechanical reinforcements in structural adhesive bonds. In this part of the research, we identified an appropriate dispersion methodology to achieve a uniform distribution of the nanotubes in the epoxy matrix and evaluated its mechanical properties. Scanning electron and transmission electron microscopy techniques were routinely used to characterize the quality of the dispersion, the geometrical properties of the nanotubes, and the fracture surfaces of the test specimens.
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<tr>
<td>3D</td>
<td>Three-dimensional</td>
<td>PA6</td>
<td>Polyamide – 6 (Nylon 6)</td>
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<td>ABC</td>
<td>Atomistic-based continuum</td>
<td>PANI</td>
<td>Polyaniline</td>
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<td>AFM</td>
<td>Atomic force microscopy</td>
<td>PE</td>
<td>Polyethylene</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
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<td>DCB</td>
<td>Double cantilever beam</td>
<td>PmPV</td>
<td>Poly-m-phenylenevinylene</td>
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<td>DGEBA</td>
<td>Diglycidyl ether of bisphenol A</td>
<td>PS</td>
<td>Polystyrene</td>
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<td>DLS</td>
<td>Double lap shear</td>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
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<td>DWCNT</td>
<td>Double-walled carbon nanotube</td>
<td>QM</td>
<td>Quantum mechanics</td>
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<tr>
<td>FEM</td>
<td>Finite element method</td>
<td>RVE</td>
<td>Representative volume element</td>
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<td>GLARE</td>
<td>Glass Laminate Aluminum</td>
<td>SAB</td>
<td>Structural adhesive bond</td>
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<td></td>
<td>Reinforced Epoxy</td>
<td></td>
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<tr>
<td>HPC</td>
<td>High powered computing</td>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>ISS</td>
<td>Interfacial shear strength</td>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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<td>Lennard-Jones potential</td>
<td>SWCNT</td>
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<td>TETA</td>
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<td>Multi-walled carbon nanotube</td>
<td>vdW</td>
<td>van der Waals</td>
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Chapter 1
Introduction and Justification

Summary: In this chapter, we define the problem, justify the undertaking of the study and outline the method of approach adopted in achieving the set objectives. Furthermore, we provide a summary of the layout of the thesis.

1.1 Paradigm shift in Composite and Airframe Design

Composite materials now represent a growing percentage of the materials used to fabricate structural components in the transportation sector. The aerospace industry in particular has become a large driving force for the growth in composite usage. Often the aerospace industry will take the lead in incorporating new technologies into their manufacturing system and then other industries (automotive, for example) will follow. For example, 22% of the primary structures in the Airbus A380 are made from GLARE or “Glass Laminate Aluminum Reinforced Epoxy”, a metal-fiber laminate consisting of alternating layers of aluminum and sheets of glass-epoxy prepeg [1]. GLARE is featured in the front fairing, upper fuselage shells, crown and side panels and the upper sections of the forward and aft upper fuselage and offers a weight savings of between 15 and 30 percent over aluminum alloy [2]. The Boeing 787 (Dreamliner), on the other hand, contains some 50% of carbon fiber reinforced plastic (CFRP) in its design [3] which translates into an average weight savings of 20% [4]. This includes practically the entire outer fuselage as depicted in Fig. 1.1. These composites are also used in the design and fabrication of the stabilisers, rudders, rotor blades, spoilers and motor casings, to name just a few. The growing demand for composite materials can be directly attributed to the need for fuel efficient design solutions in these industries. Apart from the obvious fact that lighter aircraft and automobiles translate into less fuel consumption and hence reduced air pollution, they also offer high strength, reduced weight, corrosion resistance, enhanced damage tolerance and improved fatigue resistance when compared with traditional metallic alloys such as aluminum and steel.
With the increased use of composite materials in the aerospace industry, designers are faced with the challenge of choosing an appropriate joining methodology. The use of composite laminates in the transport industry relies heavily upon the ability to provide a strong interface between the mating composite substrates. A variety of joining methods can be used to provide the assembly function. These include welding, brazing and soldering, mechanical fastening, and finally adhesive bonding. However, in many applications involving composite substrates, adhesive bonding is the only logical choice. At present, it is impossible to weld, solder, or braze composite materials together or to dissimilar materials. Mechanical fastening, on the other hand, has a number of serious disadvantages that jeopardize the structural integrity of the final product. For example, mechanical fasteners provide points of attachment in small discrete areas leading to possible high stress concentrations. In such cases, substrates may need to be thicker to handle the concentrated stress, thereby adding weight and cost to the final product. In addition, unlike rivets or bolts, adhesives produce smooth contours that are aerodynamically beneficial. Below we list some of the key advantages of using adhesive bonding as a joining methodology:

i. a better distribution of stresses over the entire bonded area,
ii. ability to optimize the geometry of a joint,
iii. ability to bond dissimilar materials,
iv. reduced weight of assembly,
v. damps vibration and absorbs shock,
vi. provides smooth contours, and
vii. less expensive and faster than mechanical fastening.

Clearly, adhesive bonding is an attractive alternative to the traditional techniques when joining composite materials. Adhesives are now used to fabricate a variety of structural and non-
structural components in aircraft. Structural adhesives, especially, account for the largest market share of all the adhesives used in aerospace applications. Figure 1.2 shows a schematic of some of the bonded areas in a modern aircraft. It is without a doubt that the growing use of composite materials has, in turn, brought adhesive bonding to the forefront in aircraft assembly. In fact, the transportation market has shown a growing trend in the use of adhesives. Over the period of 2003 to 2008 the transportation market has shown an 11% increase in the use of adhesives with some market analysts predicting a 3-4% annual growth through to 2013 [6]. However, adhesive bonding is not without its disadvantages. When compared with the adherent materials, the adhesive bonding layer generally offers a lower level of mechanical strength and fracture toughness, especially at elevated temperatures and long-term loadings. In some cases, whilst strength considerations can be met, toughness requirements are seldom satisfied. This may be due to the complexity of the bonding process and geometry, the presence of porosities, micro-defects, incomplete wetting and second-phase particles in the adhesive layer. The stringent strength and toughness requirements of the aerospace industry necessitate the reinforcement of the adhesive layer.

Figure 1.2 Adhesively bonded areas in modern aircraft (From Ref. [7]).
1.2 Justification of the Study

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 adhesive bonds (SABs). They included the addition of carbon, nylon or glass micro-fibres, rubber and liquid rubber precipitates, reactive ductile diluents and inorganic hybrid particles, among others. Whilst some improvements in bond properties have been observed [8,9], these additives also led to reductions in high temperature service capabilities, low impact strength, and poor shrinkage characteristics [10]. 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 [11]. 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 [12]. 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/cm³), and large aspect ratios (1000s). 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 SABs requires rigorous characterization and analysis. Excellent nanotube 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 numerical. 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 mechanical properties of nano-reinforced composite systems. There are a variety of modeling methods in use, which aim not only to simulate material behavior at a particular scale of interest but also to assist in developing new materials with highly desirable properties. These scales can range from the basic atomistic to the much coarser continuum levels. Individually, each of these techniques is accurate and best suited for its own length scale. However, modeling inaccuracies can arise from the improper enforcement of a specific technique on other length scales. Furthermore, it would not only be impractical but also very costly to attempt to model an entire continuum using atomistic techniques simply due to the size of the problem and the number of degrees of freedom involved. Many engineering problems are characterized in terms of multiple scales and require a novel approach to describe their behavior. In this thesis, we overcome these difficulties by developing a novel multiscale modeling technique that is capable of simulating the behavior of nano-reinforced composite materials.

1.3 Objective of the Study

It is therefore the objective of this research study to:

(i) develop a new model to study the mechanisms associated with the effect of the homogeneous dispersion of nanofillers upon the mechanical behaviour of nano-reinforced adhesives using atomistic based continuum (ABC) multiscale modelling techniques,

(ii) conduct micromechanical analysis of the stress distributions of nano-reinforced structural adhesives using a new representative volume element (RVE) that accounts for nonlinearities in the constitutive formulations of the constituents,

(iii) identify a dispersion methodology that ensures a uniform and homogeneous distribution of
the reinforcing CNTs in the adhesives considered, and

(iv) establish experimentally, via the appropriate mechanical testing, the relative merits of CNTs as reinforcements upon the mechanical properties of the newly developed nano-reinforced SABs.

1.4 Method of Approach

In this research, we focus our efforts on predicting the mechanical properties and the constitutive response of nano-reinforced SABs through the development of an ABC multiscale model. It is further our intention to validate the work experimentally. Figure 1.3 decomposes the research program into both theoretical and experimental components.

![Figure 1.3 Multiscale modeling of nano-reinforced SABs research program.](image)

The theoretical work is based on the development and analysis of a RVE. The RVE embodies the basic constituents of the nano-reinforced structural adhesive, namely; the reinforcing CNT, the surrounding adhesive matrix, and the CNT-adhesive interface. This model takes into account the discrete nature of the atomic interactions at the nanometer length scale through the notion that atomic bonds between two atoms act like load-bearing continuum elements, whereas individual atoms act as nodes of the related structure. In this multiscale model, the finite element constitutive relations are derived solely from atomistic formulations. Specifically, the Modified Morse interatomic potential will be used to describe the covalent bonding mechanisms in the CNT structure and the Lennard-Jones (LJ) potential will be used to describe the van der Waals (vdW) interactions between neighboring atoms. The constitutive response of CNTs with different structural geometries (armchair and zigzag) and their nano-reinforced adhesive equivalents will be considered and presented. Molecular dynamic simulations will accompany the predicted results as a validation tool of the proposed model. Furthermore, nanotube pull-out simulations
will be conducted to determine the interfacial properties between the CNT and the surrounding adhesive.

It is important to note that several issues pertaining to the alignment, aspect ratio, dispersion, orientation and concentration of the CNTs need to be considered and optimized in order to attain the best properties of the composite. To investigate the effects of such parameters on the effective averaged mechanical properties of the nano-reinforced adhesive, we will employ a homogenization procedure to transform the RVE into a continuous effective fiber. The representative fiber serves as a means for incorporating micromechanical analyses for the prediction of bulk mechanical properties of nano-reinforced composites with various CNT aspect ratios, concentrations, and orientations. These micromechanical investigations will be of both analytical and numerical form. The analytical approach will provide us with the elastic response of the nano-reinforced composite while the numerical simulations will offer us the ability to predict the full constitutive response for homogeneous CNT dispersions. Figure 1.4 provides a schematic illustration of the analysis process.

The experimental work is subdivided into two components; (i) the development of a dispersion methodology that ensures a uniform distribution of the reinforcing CNTs in the adhesives considered and (ii) the characterization of the mechanical properties of nano-reinforced SABs. Of critical importance in the use of CNTs as mechanical reinforcements in structural adhesives is their homogeneous dispersion in the matrix phase. CNTs have extremely high specific surface areas and large aspect ratios. This leads to two counteracting effects, one desirable offering increased stress transfer and the other undesirable leading to strong attractive van der Walls forces between the nanofillers resulting in excessive agglomeration. The resulting aggregates act as defect sites rather than reinforcements. Therefore it is of critical importance to breakup these
agglomerates. Here, we will investigate three mechanical dispersion techniques, namely; ultrasonication, calandering, and microfluidizing and identify the best route for our chosen material system. In addition, we will consider using compatible surfactants (Polyvinyl Pyrrolidone) in order to further assist in achieving a uniform and stable dispersion. The quality of the resulting dispersions will be assessed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques.

The mechanical characterization of the newly developed nano-reinforced SABs requires careful attention when fabricating the test specimens. Consideration will be given to the layup of the substrates, degassing and curing of the adhesive, and surface preparation. The chosen adhesive system will be comprised of a virgin two-component structural epoxy based on a diglycidyl ether of bisphenol A (DGEBA) and triethylene tetramine (TETA) formulation. Multi-walled (MWCNT) carbon nanotubes will be used as nanofillers and bond-line thickness control studies will be conducted using 0.1 – 0.4 mm glass beads. Accordingly, comprehensive tensile, shear, and fracture toughness test programs will be used to study the mechanical behaviour and fracture characteristics of the nano-reinforced SABs. These tests will characterize the strength and toughness of the material, the properties of the adhesive layer and the interface, and the influence of CNT reinforcement upon the failure mechanisms.

1.5 Layout of Thesis

This thesis is divided into eight chapters. Following this brief introduction, Chapter 2 provides a critical review of the relevant works in three main areas: (i) carbon nanotubes and nanocomposites, (ii) mechanical characterization of nanocomposites, and (iii) multiscale modeling and theoretical characterization of nanocomposites. Chapter 3 provides details of the multiscale modeling of nano-reinforced structural adhesive bonds and the governing formulations as they pertain to the atomistic-based continuum method and molecular dynamic validations. Chapter 4 discusses how the proposed model is extended to investigate the interfacial properties between the reinforcing CNT and surrounding adhesive. Chapter 5 outlines the micromechanical techniques and formulations used to predict the bulk effective mechanical properties of the newly developed adhesive. Chapter 6 describes the experimental investigations including the materials used, specimen preparation, experimental setup and dispersion methodology. Chapter 7 is devoted to the analysis of the results and discussions. Finally, in
Chapter 8 we conclude the work and identify the original contributions of the thesis and outline suggestions for related future research.
Chapter 2
Literature Review

Summary: This literature review is divided into four main sections. The first addresses the structure and mechanical properties of CNTs and their potential application as nanofillers. The second deals with the importance of dispersion and the techniques used to develop nano-reinforced composites and their mechanical characterization from an experimental viewpoint. The third section addresses the different theoretical techniques used to characterize nanocomposites containing CNTs with an emphasis on multiscale modeling. Finally, in the last section, we identify the need for the current studies.

2.1 Carbon Nanotubes

Carbon nanotubes exhibit a remarkable combination of mechanical, electrical and thermal properties. Many potentially important applications have been explored, including the use of nanotubes as nanoprobe tips [13], field emitters [14-17], storage or filtering media [18], and nanoscale electronic devices [19-23] to name a just a few. Their discovery together with earlier theoretical predictions of a nano ‘supermaterial’ stimulated enormous interest in the field of nanomaterials. A large percentage of academic and popular literature attributes the discovery of CNTs to Iijima in 1991 [24]. However, there are several papers published well before that time that identified the nanoscale carbonaceous fibers in several controlled experiments [25-27]. It is, however, Iijima who is responsible for reporting the structural perfections of CNTs, and hence, implied the extraordinary properties that have been realized today.

2.1.1 Structure of CNTs

Carbon nanotubes occur in two general forms; SWCNTs and MWCNTs. SWCNTs can generally be visualized as a single sheet of graphene that has been rolled into a hollow tubular shape. The orientation of the graphene sheet as it is rolled will dictate the resulting structure of the CNT. SWCNTs can have diameters as small as 0.4 nm and normally no larger than 2 nm. MWCNTs can be viewed as several concentric SWCNTs with outside diameters that range between 5 nm and 100 nm. The interlayer spacing of MWCNTs is approximately 0.34 nm [28,29] and this value is also widely taken as the thickness of individual CNT layers in numerical simulations.
[30-33] and in some experimental investigations [34,35]. Figure 2.1 depicts both the SWCNT and MWCNT structures.

![Figure 2.1 Two CNT variants: (a) a SWCNT and (b) a MWCNT.](image)

A schematic illustration of an unrolled graphene sheet is shown in Fig. 2.2. CNTs are defined by a pair of indices (n,m) which are used to identify their atomic structure and size. These indices correspond to a lattice vector \( \mathbf{R} = n\mathbf{r}_1 + m\mathbf{r}_2 \) on the graphene plane, where \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) are unit vectors in the hexagonal lattice, and \( n \) and \( m \) are integers. This lattice vector maps onto the circumference of the resulting nanotube cylinder. The orientation of the graphite lattice relative to the longitudinal axis defines the chirality or helicity of the nanotube [36]. Two main symmetry groups exist: armchair \((n,n)\) and zigzag \((n,0)\) configurations, with all other \((n,m)\) combinations referred to as chiral nanotubes.

![Figure 2.2 Unrolled graphene sheet and the chiral lattice vector.](image)
A noticeable feature of the graphene sheet is the hexagonal pattern which is repeated periodically in space. Each carbon atom in the lattice is covalently bonded to three neighboring atoms. This hexagonal structure is attributed to the sp² hybridization process. One s-orbital and two p-orbitals of a carbon atom in its excited state combine to form three hybrid sp² orbitals at 120 degrees relative to each other. This sp² hybridization process is illustrated in Fig. 2.3. The resulting covalent bond, known also as a σ-bond, is a strong chemical bond which is largely responsible for the unique properties of CNTs. The other relatively weak out-of-plane bond, known as the π-bond, is typically exploited in functionalization processes, which involve the grafting of functional groups on the walls of CNTs as a means of improving their interfacial bonding with a surrounding polymer matrix.

![Figure 2.3 The sp² hybridization process and the resulting σ- and π-bonds.](image)

### 2.1.2 Mechanical Properties

Early theoretical and experimental work has confirmed that CNTs possess exceptional mechanical properties. To date, a number of researchers have employed both experimental and theoretical techniques to determine the mechanical properties of CNTs. However, due to the extremely small size of CNTs, the experimental studies are challenging and the results normally show significant variability. This could also be attributed to differences in the CNT structure, existing defects and synthesis techniques. Experimental techniques approximate CNTs as elastic structural members, and in so doing, impose continuum assumptions. As a consequence, the experimental measurements are faced with the problem of defining the cross-sectional area of the CNTs. Most approaches approximate the cross-sectional area to be equal to that of a hollow thin walled cylinder; namely, πdt where t is taken as the interlayer spacing of graphene [34, 35].

Although the testing of individual nanotubes is a challenging task, a number of techniques have been developed to provide insights into their mechanical behavior and to quantify these
properties. The experimental techniques used range from direct tensile loading measurements to techniques based on observing their freestanding room temperature vibrations in a TEM. For example, Lourie and Wagner [37] measured the cooling-induced compressive response of CNTs using micro-Raman spectroscopy. Young’s modulus of both SWCNTs and MWCNTs were then derived from a concentric cylinder model involving thermal stresses. In their study, Lourie and Wagner reported Young’s moduli of 2.8 to 3.6 TPa and 1.7 to 2.4 TPa for SWCNT and MWCNT, respectively. In comparison, Yu et al. [35,38] determined the Young’s modulus to range from 320 to 1470 GPa and 270 to 950 GPa for SWCNT ropes and individual MWCNT, respectively, using atomic force microscopy (AFM). Figure 2.4 shows SEM images of the SWCNT rope (multitudes of entangled CNTs) tensile-loading experiment conducted by Yu et al. where both pre- and post- loaded CNTs are depicted. Several experimental reports of Young’s modulus values for both SWCNTs and MWCNTs are provided in Table 2-1 along with their respective references and details of their methodology.

![Figure 2.4 SEM images showing a SWCNT rope under direct tensile loading using AFM (From Ref. [35]).](image)

<table>
<thead>
<tr>
<th>Author</th>
<th>Technique</th>
<th>CNT Type</th>
<th>Young’s Modulus</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lourie and Wagner</td>
<td>Micro-Raman Spectroscopy</td>
<td>SWCNT</td>
<td>2.8 – 3.6 TPa</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MWCNT</td>
<td>1.7 – 2.4 TPa</td>
<td></td>
</tr>
<tr>
<td>Yu et al.</td>
<td>AFM</td>
<td>SWCNT rope</td>
<td>320 – 1470 GPa</td>
<td>[35,38]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MWCNT</td>
<td>270 – 950 GPa</td>
<td></td>
</tr>
<tr>
<td>Tombler et al.</td>
<td>AFM</td>
<td>SWCNT</td>
<td>1.2 TPa</td>
<td>[34]</td>
</tr>
<tr>
<td>Krishnan et al.</td>
<td>TEM / vibrational theory</td>
<td>SWCNT</td>
<td>0.9 – 1.7 TPa</td>
<td>[39]</td>
</tr>
<tr>
<td>Salvetat et al.</td>
<td>AFM</td>
<td>SWCNT rope</td>
<td>0.81 +/- 0.41 TPa</td>
<td>[40]</td>
</tr>
</tbody>
</table>
Experimental measurements of the tensile strengths of CNTs have also been conducted. However, they are limited due to the difficulties associated with the application of direct tensile loads on individual CNTs. The tensile strengths of SWCNT ropes were investigated by Walter et al. [41] via AFM. They assumed Young’s modulus of 1.25 TPa in their calculations, and in so doing obtained an average tensile strength of 45 GPa. In the study by Yu et al. [38], the tensile strengths of MWCNTs ranged from 11 to 63 GPa. The MWCNTs were also shown to fail via a sword-and-sheath type mechanism, where the outer layer first fractured and the inner layers were subsequently pulled out. Weak load transfer was observed between the inner and outer layers of the MWCNT with interfacial shear strengths (ISS) of 0.08 MPa and 0.3 MPa arising from the weak vdW interactions between the subsequent layers. The weak load transfer between the subsequent layers was also demonstrated by Cumings and Zettl [42]. They used a movable nanomanipulator inside a high-resolution TEM to withdraw the inner layer of a MWCNT from its surrounding outer layer. The measured interfacial shear strength arising from the van der Walls interactions was determined to be in the range of 0.43 to 0.66 MPa. They also demonstrated controlled and reversible telescopic extension of MWCNTs whereby the inner layer is withdrawn under direct loading and upon removal of the load it retracts back as a result of the attractive vdW interactions.

Researchers have used modeling methods accounting for all length scales to characterize the behavior of CNTs. First principle quantum mechanical descriptions have been employed to model the structural deformation [43], fracture [44], defect nucleation [45], chemical reactivity [46,47], and functionalization [48,49] of individual CNTs. Classical molecular dynamic and molecular mechanic simulations have been shown to play an important role in determining the constitutive relations of CNTs under different loading conditions [50-52], CNT growth mechanisms [53], oscillatory properties [54], and the effects of chirality and length on the mechanical properties [55]. At the coarser end of the length scale, continuum mechanical concepts have also been used in characterizing CNT behavior. In continuum based approaches, the CNT is modeled as a continuous shell with a fixed wall thickness and material properties [56-58]. However, the only way of distinguishing between nanotubes of different chirality (zigzag, armchair, chiral) is through the radius of the shell. The disadvantages of this approach are that the CNT is drastically oversimplified, it cannot be used to study the effect of defects, and the atomic structure of the CNT has been ignored. Nevertheless, continuum based approaches have
been shown to reasonably predict the tensile and shear moduli of individual CNTs [59,60] and their deformation and stability under different loads [61-63]. Additionally, a number of multiscale approaches have also been pursued [64]. The theoretical predictions tend to overestimate the mechanical properties when compared to experimental findings which assume that the CNT is a defect-free structure. At the same time, it is easier to investigate the effect of such parameters as temperature, strain rate, defect nucleation, chirality, size, and different loading conditions in theoretical approaches. In this context, the elastic properties of CNTs are rarely presented as single values but rather as varying functions of the diameter or chirality. Due to the sheer number of theoretical efforts made in this field, the reader is referred to a review by Ruoff et al. [65] for further details.

2.2 Nano-Reinforced Composites

In this thesis, we limit our analysis to the use of CNTs as a filler phase for structural reinforcement in a host polymer. The general term *nano-reinforced composite* or *nanocomposite* can be used to reflect any composite material with a reinforcing phase exhibiting a characteristic dimension below 100 nm. In fact, nanofillers such as carbon blacks, silicas, boron nitride nanotubes, graphite nanoplatelets, nanoclays and nanowires have been incorporated into a variety of host materials such as polymers, ceramics, and metallic matrices constituting a nanocomposite material. However, the focus of this thesis is on the nano-tailoring of the mechanical properties of structural adhesives through the homogeneous dispersion of CNTs. Recent work in this area shows that the scientific community is adopting a variety of different methods to develop these nano-reinforced composites with varying levels of success. The properties of CNT-based nanocomposites are influenced by a number of factors that include the CNT synthesis and purification process, the geometrical and structural properties of the CNTs, their alignment in the matrix, the dispersion process, and the fabrication process. In the following sections, we will discuss the techniques used to disperse CNTs in polymeric matrices, the different functionalization processes which ultimately lead to more stable CNT solutions and the experimental investigations into the mechanical properties of CNT polymer nanocomposites.

2.2.1 Dispersion and Functionalization

One of the most important aspects to consider in the fabrication of polymer nanocomposites is the homogeneous dispersion of the nanofillers into the polymeric matrix. The ultimate goal of
the dispersion process is to break up nanotube agglomerates and homogeneously distribute the individual CNTs throughout the matrix. CNTs tend to exhibit an enormous surface area being several orders of magnitude larger than the surface of conventional fillers. The large surface area of CNTs can lead to excessive agglomeration due to increased intermolecular interactions. Van der Waals forces are the weakest type of intermolecular forces and are created by the attraction between induced dipoles in a nonpolar molecule. The vdW interactions between CNTs are notably larger than vdW interactions between polymer chains because of the absence of hydrogen atoms. This attraction coupled with their nanoscopic size and high aspect ratios lead to considerable aggregation. The resulting aggregates act as defect sites rather than reinforcements, leading to a degradation in the properties of the nanocomposite [66]. An efficient utilization of the CNT properties in polymeric materials is therefore related to their homogenous dispersion in the matrix. Of equal importance is the stability of the resulting dispersion. It is desirable that the CNTs remain in their uniformly dispersed state after processing and not re-agglomerate as a result of their attractive interactions.

The dispersion, aggregation, agglomeration and entanglement of CNTs are a subject of current intensive research [67-70]. Most strategies combine the use of mechanical and chemical routes. The mechanical routes include high-shearing techniques using mechanical stirring, sonication, microfluidizing, and calendaring. These methods involve imposing high shear forces on the CNT/polymer mixture that leads to the homogeneous dispersion of the CNTs. Chemical strategies, on the other hand, typically involve either covalent modification of the surface of the CNT, or the use of a dispersant or surfactant; being polymeric or supramolecular in nature. The chemical strategies are more effective in preventing the reagglomeration of the CNTs after the dispersion process has been carried out.

The mechanical techniques all rely on imposing high shear stresses on the CNT polymer mixture as a means of exfoliating the agglomerates and allowing the polymer molecules to appropriately wet the CNTs. Mechanical stirring is normally used as a means of producing a pre-mixture or preliminary dispersion that is subsequently employed in the other techniques. The mechanical stirring operation is normally carried out using a mixing device at relatively high revolutions (about 1000 rpm). The size and shape of the propeller and the mixing speed control the resulting dispersion. The resulting pre-mixture is then used with either of the remaining techniques to further disperse the CNTs.
Ultrasonication is a common technique widely used either on its own or in combination with other processes to disperse nanotubes into polymer matrices. It uses high frequency sound waves to induce the separation of CNT agglomerates. It operates on the principle of inertial cavitation with the rapid formation and violent collapse of a void or bubble in the liquid producing intense shearing forces. When sonicating liquids at high intensities, the sound waves that propagate throughout the media result in alternating high-pressure and low-pressure cycles. During the low-pressure cycle, the high-intensity waves form small vacuum bubbles in the liquid. When the bubbles attain a volume at which they can no longer absorb energy they implode producing a shockwave. This process is schematically illustrated in Fig. 2.5. Both the time and frequency of the sonication process will affect the resulting dispersion. Ultrasonic instruments using a frequency of 20 kHz have been shown to homogeneously disperse MWCNT mats [71]. Kearns and Shambaugh [72] report an optimum sonication time of 2 hrs for a 1 wt% CNT concentration in a polypropylene solution.

The calendaring or three-roll mill approach relies on processing the mixture through three horizontally positioned rolls all rotating at different angular velocities and in opposite directions relative to one another. Figure 2.6 shows a schematic of the general configuration of this method. The mismatch in the roller velocities coupled with a very small gap between the rollers results in high shear stresses. This approach offers nearly pure shearing as compared to other milling techniques which also rely on compressive stresses to induce separation. As such it does not significantly degrade the nanotubes. This technique has recently been applied by a number of research groups reporting excellent dispersions [73-76]. In contrast, the microfluidizer approach
relies on forcing the mixture through a very narrow (100 μm) Z-shaped channel at high speeds (500m/s) to impose the shear stresses [77]. This technique has been used in a number of chemical, medical, pharmaceutical and cosmetic applications, but has just recently been viewed as an alternative to the existing mechanical CNT dispersion techniques.

Some of the above techniques may initially break up the agglomerates but are incapable of creating a stable solution that prevents the re-agglomeration of the nanofillers especially in low viscous mediums [78,79]. In these specific cases it is desirable to combine the mechanical techniques with chemical methods. Chemical strategies improve the stability of the CNT polymer solution and prevent their re-agglomeration which ultimately leads to a better dispersion when coupled with the mechanical techniques. Furthermore, these techniques also improve the load transfer and interfacial bonding between the CNTs and surrounding polymer. Two approaches are generally available when using chemical methods to aid in the dispersion of CNTs in a polymeric matrix. The first is non-covalent functionalization which refers to the adsorption of surfactant molecules or the helical wrapping of polymer molecules on the CNT walls. This is realized by using conjugated polymers, which can associate with the CNTs by means of π-π electronic interactions with the CNT lattice. This results in the helical wrapping of polymer chains around the CNT which in turn improves the wetting of the CNTs by the polymer. The helical wrapping of the polymer chain has been observed experimentally [80]. This form of functionalization is particularly attractive because it provides an opportunity to attach a large number of functional groups on the walls of CNTs without introducing structural defects. These functional groups prevent the individual CNTs from attracting one another by separating them sufficiently such that the vdW interactions cannot act between them. Hence, this technique prevents the formation of agglomerates and improves the dispersability of the CNTs [81].
surfactants are used in this approach they have the additional benefit of effectively imposing repulsive electrostatic forces on the neighboring nanotubes aiding their separation. The second approach is called covalent functionalization or chemical cross-linking. In this case, a small percentage of strong covalent bonds form from the grafting of functional groups on the CNT walls. Therefore, unlike non-covalent functionalization which relies on the wrapping of a polymer chain with functional groups mounted on the backbone, covalent functionalization directly grafts the functional groups on the exterior walls of the CNT.

2.2.2 Experimental Investigations of the Mechanical Properties

When the structural perfections of the CNT were first reported by Ijiima in 1991 [24], there was much speculation that these carbonaceous fibers could be the strongest known materials. Since that time the outstanding mechanical properties of CNTs have indeed been verified and they are now being viewed as the most promising reinforcing agents in high-performance composite materials for a variety of structural applications. Consequently, there have been numerous efforts by researchers from laboratories all over the world to realize these outstanding improvements in the mechanical properties of a variety of different host polymeric matrices. Therefore, this section will primarily address the most recent and significant improvements in strength, stiffness, and fracture toughness of structural adhesives available in literature.

Nanocomposite Strength and Stiffness

The enhancement of the modulus of a polymer reflects the ability to transfer stress from the polymer matrix to the high modulus CNTs. Therefore, strong interfacial adhesion between the polymer and CNT is preferred for stiffening of the composite. An enhancement in the strength of a polymer also reflects strong interaction between the polymer and CNTs, however, strength is also affected by the presence of defects, voids, agglomerates, and other inclusions, which serve to initiate fracture. The published experimental data show that the tensile stiffness of CNT composites is generally improved, however, a comparison of the data is difficult given the significant variability in processing techniques, types of CNTs, surface treatments, polymer matrices, and test methods that have been used. The enhancement in stiffness is usually most prominent in the low CNT weight fractions. With regards to reinforcing polymeric matrices with CNTs to improve their strength and stiffness, both MWCNTs and SWCNTs have been used with varied levels of success. MWCNTs are generally preferred due to their relatively lower
production cost, however, the internal layers of MWCNTs tend to slide within one another and undermine the load bearing capability of the nanotubes; only the outer shell of MWCNTs tend to carry the load. This is because only weak vdW interactions transfer loads between the neighboring shells. As a result the inner layers can rotate and slide freely.

Perhaps the most remarkable improvement in both the tensile modulus and yield strength of a polymer through the dispersion of CNTs was observed by Liu et al. [82]. By dispersing only 2 wt% MWCNTs in a nylon-6 (PA6) matrix Liu et al. observed an increase of approximately 214% in the tensile modulus and 162% in the yield strength. The MWCNTs were first purified by dissolving a catalyst in hydrochloric acid followed by refluxing in 2.6 M nitric acid as a means of increasing more carboxylic and hydroxyl groups. Composite samples then were prepared via a melt-compounding method. They attributed these impressive improvements in the stiffness and strength to a uniform and fine dispersion of the CNTs and good interfacial adhesion between the nanotubes and matrix which were assessed using SEM. In contrast, Liu et al. [83] also used the melt compounding method to fabricate MWCNT/PA6 composite specimens. The MWCNTs used in their study were synthesis in ethanol flame which was shown, through the use of a variety of microscopy techniques, to produce active functional groups on the surface of the MWCNTs. These MWCNTs were further functionalized with n-Hexadecylamine molecules. Through the use of SEM, they concluded a uniform dispersion and good wetting with the PA6 matrix. However, the observed improvements in the tensile modulus and tensile strength were only approximately 29% and 6%, for cases involving 1 wt% CNTs, respectively. In another recent study, Sahoo et al. [84] dispersed carboxyl-functionalized MWCNTs in a PA6 matrix. They used two both an internal mixer and an extrusion process to disperse the CNTs in the PA6 matrix. They observed a maximum increase of approximately 126% in the tensile strength when 10 wt% of the functionalized MWCNTs were incorporated in the PA6 matrix. This clearly demonstrates a significant variability in the results of three separate experimental studies that used the same fabrication method, constituent materials and both claiming uniform dispersions and good wetting with differences only in the pretreatment processes of the MWCNTs. It is anticipated that while the ethanol flame CNT synthesis method can produce CNTs with inherent functional groups it may also introduce considerable defects in the walls of the CNTs which may help explain the significantly lower improvements observed by Liu et al. [83].
Gojny et al. [85] investigated the mechanical properties of an epoxy reinforced with both non-functionalized and amino-functionalized CNTs. One of the objectives of the study was to identify the best nanofiller when SWCNTs, double-walled carbon nanotubes (DWCNTs), and MWCNTs were considered. The nanocomposites were produced using the same processing conditions and systematically varying CNT type, content, and surface functionality. The CNTs were dispersed in the two component epoxy system using the calandering approach following by intense mixing with the hardening agent. TEM micrographs seemed to confirm a uniform dispersion of the CNTs with fewer agglomerates observed in the case of DWCNTs and MWCNTs as these nanofillers tend to exhibit lower specific surface areas when compared with SWCNTs. In all cases amino-functionalized CNTs produced better results when compared with non-functionalized CNTs which can be attributed to the better interfacial adhesion of the CNTs and epoxy and the improved dispersion. The results showed that the greatest improvements in both tensile modulus and strength were observed for the amino-functionalized DWCNTs at concentrations of about 0.5 wt% with improvements of approximately 14.5% and 8.4%, respectively. It was expected that SWCNTs would provide the highest improvement in these properties given that these fillers have the largest specific surface area and aspect ratio, however, the DWCNTs did not agglomerate as pronounced as SWCNTs. In general, MWCNTs, whether functionalized or not, actually degraded the tensile modulus and tensile strength over that of the pure epoxy. This was attributed to the absence of stress transfer between the internal layers of the MWCNTs, and the relatively low specific surface area and aspect ratio present. Figure 2.7 (a) to (d) summarize these results. In a more recent study by Guo et al. [86], MWCNTs were functionalized through a nitro sulfuric acid treatment and dispersed in an epoxy using a sonication technique. They observed a 35.5% increase in the tensile modulus and a 10% increase in the tensile strength when the epoxy was reinforced with 3 wt% functionalized MWCNTs.
Figure 2.7 A comparison of the (a) ultimate tensile strength of epoxy-based nanocomposites containing nonfunctionalized nanotubes and (b) functionalized nanotubes and (c) the Young's modulus of epoxy-based nanocomposites containing nonfunctionalized nanotubes and (d) functionalized nanotubes (From Ref. [85]).

**Fracture Toughness of Nanocomposites**

Polymeric resins such as epoxies, which are extensively used as the matrix phase in advanced composite structures, provide excellent strength, stiffness, thermal stability, chemical and environmental resistivity but possess relatively low toughness. Improving the fracture toughness of brittle polymers such as epoxies has the potential to significantly improve the service life of products made from composite materials. The stringent requirements of a number of industries, such as aerospace and automotive, necessitate the reinforcement of these materials. A number of techniques have been considered to improve the fracture toughness of epoxies. They include the formulation and modification with other materials such as the addition of carbon, nylon or glass microfibers, rubber, liquid rubber and rubber precipitates, reactive ductile diluents and inorganic...
hybrid particles, among others. Whilst some improvements in bond properties have been observed [87,88], these additives can also lead to reductions in high temperature service capabilities, low impact strength, sensitivity to moisture, and poor shrinkage characteristics [89]. For example, a common method of toughening epoxy adhesives is blending the primary resin with other polymers, such as thermoplastics and elastomers. However, this technique usually combines both the good and bad characteristics of each resin system. Epoxy-nylon adhesives provide a major improvement in toughness over a pure epoxy formulation, but they have sensitivity to moisture because of the nylon constituent. Elastomeric particles such as rubber have also been used to toughen adhesives. The rubber inclusions absorb energy and stop cracks from propagating throughout the bondline. However, rubber-based adhesives have low glass transition temperatures. The addition of heat will soften the adhesive and directly affect its function. In all the above hybrid systems, the added toughening resin reduces the overall glass transition temperature of the system, thereby reducing elevated temperature performance and environmental resistance [89]. In an effort to improve the fracture toughness of polymers, at little or no cost to other properties, a number of researchers have attempted to use nanofillers such as CNTs which have actually been shown to improve secondary aspects as well, such as the glass transition temperature and thermal stability [84,90,91]. Based on the experimental results, the reinforcement of brittle polymers such as epoxies through the homogeneous dispersion of CNTs has resulted in significant improvements in fracture toughness, when compared to the neat polymer system. As a result of this experimental data, investigations into the dominant toughening mechanisms associated with these improvements have begun.

Several experimental efforts have been made to improve the fracture toughness of polymer systems through the homogeneous dispersion of CNTs. Gojny et al. [73] examined the fracture toughness of CNT/epoxy composites containing functionalized and non-functionalized DWCNTs dispersed through shear mixing in an epoxy matrix. The fracture toughness for functionalized DWCNTs was found to increase by as much as 26% compared to the pure epoxy matrix, when a filler content of 1 wt% was used. Lachman and Wagner [92] investigated a multitude of different CNTs and other nanofillers as a means of improving the fracture toughness of a common epoxy. These included carbon black, carbon nanofibers, pristine MWCNTs, and two different forms on functionalized MWCNTs, namely, carboxylated and aminated. The nanofillers were dispersed in the epoxy by means of mechanical stirring and sonication. Figure
2.8 presents the results of their test. As can be seen, the carbon black and carbon nanofiber based composites showed no significant improvement in fracture toughness, whereas all CNT polymer composites displayed significantly higher fracture toughness values when compared with the pure epoxy. The toughening effect is the highest in the NH$_2$–CNT nanocomposites for which it is approximately twice the pure epoxy value when the CNTs were dispersed in ethanol prior to mixing with the epoxy.

![Figure 2.8 Measured fracture toughness values for a variety of commonly used nanofillers (From Ref. [92]).](image)

Ganguli et al [93] performed single edge notch three-point bending tests on MWCNT/epoxy specimens prepared using an asymmetric high speed mixer to disperse the nanotubes. Samples of the neat polymer as well as the composite containing 1 wt% MWCNT were prepared. The results showed that the addition of the nanotubes resulted in a 300% increase in the stress intensity factor over the pristine sample. Seyhan et al. [94] dispersed both functionalized and non-functionalized DWCNTs and MWCNTs in a modified vinyl-ester/polyester hybrid matrix using a calander approach. The functionalized CNTs were found to provide the most significant increase in fracture toughness. Specifically, the functionalized MWCNTs exhibited a 40% increase in fracture toughness at 0.3 wt% nanotube content when compared to the neat polymer. Functionalized DWCNTs exhibited a fracture toughness increase of more than 20% at 0.3 wt% nanotube content. In addition, they found that the calandering dispersion process was more
effective at homogenously dispersing MWCNTs than DWCNTs. Yu et al. [95] studied the fracture toughness of MWCNTs/epoxy composites with nanotube contents between 0 and 3 wt% using a sonication dispersion method and a degassing agent to prevent the formation of voids. A maximum increase in fracture toughness of 62-66% at 3 wt% filler content was found over the neat polymer. In comparison, the samples without the degassing agent only exhibited an increase of 29-40% at 3 wt% nanotube content. The variation in fracture toughness for samples with the same nanotube content was attributed to the duration of the sonication and stirring treatments, with higher dispersion times giving higher toughness values. The experimental results have indicated that significant increases in the fracture toughness of CNT based composites can be achieved at very low CNT contents. However, as with most of the other mechanical properties, there exists a critical CNT concentration above which the fracture toughness begins to degrade which can be attributed to the inability of present dispersion techniques to ensure de-agglomeration of CNTs at large concentrations.

The incorporation of CNTs into polymeric matrices as a means of improving the fracture toughness requires a comprehensive understanding of the toughening mechanisms associated with this class of materials. The micro toughening mechanisms in ductile and brittle solids have been extensively explored [96-98], however, the dominant mechanisms in nanocomposites require further investigation. Crack bridging and CNT pull-out have been identified as two of the main toughening mechanisms associated with this class of materials. Furthermore, fiber-pullout tests have been well recognized as the standard method for evaluating the interfacial bonding properties of composite materials. The output of these tests is the force required to de-bond the fibers from the surrounding polymer matrix and the shear stresses involved. In the case of CNT reinforced polymers, experimental tests have been conducted but are limited due to the nano-scale involved. Previous authors have reported experimental results in which the ISS was found to be within the range of 35 MPa to 376 MPa [99-101] based on CNT pull-out using a scanning probe microscope. However, shear strengths as high as 500 MPa have also been reported by Wagner and co-workers [102] based on fragmentation tests in urethane-CNT composites. Barber et al. [103] have also conducted pull-out measurements on an individual SWCNT embedded in a polymer matrix using AFM. Fielder et al. [104] obtained evidence of DWCNTs and MWCNTs bridging cracks in a low viscosity resin system using TEM and SEM micrographs. Figures 2.9 and 2.10 are reproductions of those micrographs. One can see a hollow channel in the matrix of
Fig. 2.9 providing evidence of the nanotube pull-out mechanism. Other evidence of these toughening mechanisms can be found in Prashantha et al. [105], W. Zhang et al. [106], and Thostenson and Chou [107].

2.3 Existing Multiscale Models and Theoretical Characterization of Nanocomposites

There are a variety of modeling methods in use which aim not only to simulate material behavior at a particular scale of interest but also to assist in developing new materials with highly desirable properties. These scales can range from the basic atomistic to the much coarser continuum levels. The hierarchy of modeling methods consists of quantum mechanics (QM), molecular dynamics (MD), micromechanics (MM), and finally continuum mechanics. Individually, each of these methods is accurate and best suited for its own length scale and modeling inaccuracies can arise from the improper enforcement of a specific technique associated with a particular length scale on other length scales. Furthermore, it would not only be impractical but also very costly to attempt to model an entire continuum using purely atomistic approaches due to the number of degrees of freedom involved. Many engineering problems are characterized in terms of multiple scales and require a novel approach to describe their behavior. In this case, it is carried out using multiscale computational modeling techniques which can describe the behavior of materials on scales ranging from atomistic to continuum.

To date, there have been a vast number of numerical models developed for the characterization of nanocomposites primarily because of the different modeling techniques that can be adopted.
This section will review the numerical efforts of the research community in predicting the mechanical properties of CNT-reinforced composites. This section will be divided into atomistic, continuum, and multiscale efforts due to the abundant research devoted to understanding the mechanics of these materials.

2.3.1 Atomistic Modeling

Atomistic methods, such as MD, have been extensively used to model this class of materials. In the MD approach, classical equations of motion for each atom are integrated step-wise in time. These timesteps can range from one to ten femtoseconds and the corresponding simulation times can range from several picoseconds to nanoseconds, depending on the system being investigated. Due to the number of degrees of freedom involved these approaches are generally computationally intensive and limited by the realistic system sizes that they can represent. Even the use of state-of-the-art parallel supercomputers can only handle a limited number of atoms ($\sim 10^9$), corresponding to less than one cubic micron [108,109]. Therefore, the atomistic level approaches can presently only model short nanotube segments and a small numbers of short polymer chains. Such models are normally applied in investigations related to the interfacial bonding mechanisms of CNTs with a variety of polymer systems. These include polyethylene (PE), poly-m-phenylenevinylene (PmPV), 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.

Lordi and Yao [80] studied the interfacial adhesion mechanisms of CNTs embedded in a variety of polymer matrices. They used force-field based molecular mechanics calculations to determine binding energies and sliding frictional stresses between the CNTs and surrounding polymers. The results of the study indicated that the binding energies and frictional forces only play a minor role in determining the ISS. Lordi and Yao also determined that the helical wrapping of the polymer chains in non-covalently functionalized CNTs does in fact contribute significantly to increase in the ISS. Frankland et al. [110] investigated the effect of chemical cross-linking or functionalization via MD simulations employing a many-body bond-order potential that allowed for the formation of chemical bonds and rehybridization. They considered both amorphous and crystalline PE matrices. Their simulations predicted that the ISS can be increased by over an order of magnitude from the introduction of cross-links involving less than 1% of the carbon
atoms in the nanotube structure. Higher interfacial shear stresses were observed for the crystalline composites in both non-bonded and crosslinked configurations. Furthermore, their investigation also predicted a negligible change in the tensile modulus of the CNT considered. Gou et al. [111] used both molecular mechanics and MD simulations to study the load transfer and interfacial properties of individual SWCNTs and CNT ropes. The ISS was calculated to be up to 75 MPa for a SWCNT embedded in a polymer matrix. The simulations also showed that individual CNTs have stronger interactions with the surrounding polymer and hence provide better load transfer when compared to the CNT rope. More recently, Zheng et al. [112] used both molecular mechanics and MD to study the effect of chemical functionalization on the interfacial bonding characteristics of a SWCNT embedded in a PE matrix. They investigated the effect of several different functional groups and found that the ISS can improve by as much as 1700% for cases involving 5% of the carbon atoms in the CNT functionalized with phenyl groups. Wei [113] studied the temperature dependent adhesion behavior and reinforcement effect of CNTs in a PE matrix through MD simulations. Wei only considered vdW interactions in his model and established a lower bound ISS of approximately 47 MPa which was found to be in excellent agreement with the experimental measurements of Barber et al. [114]. Liu et al. [115] used MD to investigate a hybrid system of non-covalent and covalent functionalizations. They found that the interfacial shear strength for a pristine SCNT/epoxy system was approximately 170 MPa. When non-covalently functionalized, the ISS increased to 290 MPa and to 690 MPa when covalently functionalized. Furthermore, the hybrid system resulted in an ISS of 940 MPa.

The stress-strain response of CNT-reinforced polymers was investigated using MD by Frankland et al. [116]. They considered both continuous and discontinuous SWCNTs embedded in polyethylene matrices. Frankland et al. obtained the stress-strain curves for both systems under tensile and transverse loading conditions. The long-nanotube composite showed an increase in the stiffness relative to the polymer and behaved anisotropically under the different loading conditions considered. The short-nanotube composite showed no enhancement relative to the polymer, which they attributed to the low aspect ratio of the nanotubes. The stress-strain curves obtained from the MD simulations were also compared with corresponding rule-of-mixtures predictions. Similar simulations were performed by Griebel and Hamaekers [117], where they used the Parrinello-Rahman approach to apply an external stress to the system to derive the stress-strain relations of a SWCNT polyethylene composite. Again, both short and infinite
nanotube configurations were considered. Han and Elliot [118] used MD to study the elastic moduli of a SWCNT reinforced polymer composite. Two amorphous polymer matrices were considered, PMMA and PmPV. A constant-strain energy minimization method was then applied to calculate the axial and transverse elastic moduli of the composite system. A comparison with the traditional rule-of-mixtures systems showed that for strong interfacial interactions, there can be large deviations of the results from the rule-of mixtures.

2.3.2 Continuum Modeling

The traditional framework in mechanics has always been the continuum. Under this framework, materials are assumed to be composed of an infinitely divisible continuous medium, with a constitutive relation that remains the same for a wide range of system sizes. The underlying atomic structure of matter is neglected altogether and is replaced with a continuous and homogeneous material representation. Continuum approaches have been applied to study nanoscale materials. However, traditional continuum based models cannot accurately describe the influence of the nanofillers upon the mechanical properties, bond formation/breakage and their interactions in the composite systems because they lack the appropriate constitutive relations that govern material behavior at this scale. At the nano-scale, traditional continuum mechanical concepts do not maintain their validity and gross oversimplifications can arise from the use of a purely continuum model. For example, Chang et al. [119] used molecular mechanics to show that the classic relationship between Young’s modulus and the shear modulus in the elastic theory of continuum mechanics is not retained for a SWCNT. Specifically, if the classic formula is used, they showed that the shear modulus would be well overestimated for SWCNTs with large chiral angles and underestimated for those with small chiral angles. However, the continuum approach can still provide valuable insights into the effects of such parameters as CNT curvature, aspect ratio and volume fraction on the effective mechanical properties of CNT polymer composites. Furthermore, for computational simplicity, and to adequately address scale-up issues, it is also desirable to couple atomistic models with established micromechanical techniques to describe the mechanical behavior of polymer nanocomposites on a macroscopic scale. In this case, the problem is often formulated at the atomistic level using the concept of a RVE which is subsequently homogenized into a representative fiber having uniform properties. The representative fiber is then used to describe the nanophase and its immediate surrounding in the micromechanical description.
Fisher et al. [120,121] developed a finite element model to investigate the effect of CNT waviness on the Young’s modulus of SWCNT reinforced polymers. A schematic of their model is depicted in Fig. 2.11(a). The figure clearly shows the wavy nature of the CNT and also illustrates the continuum simplification in modeling a nanotube as a thin walled cylinder where the atomic description has been ignored. The model assumed a fully bonded configuration and used a sinusoidal curvature distribution function to model different nanotube shapes in the matrix. The effective stiffness of the curved nanotube unit cell was determined and used in a micromechanical prediction of the effective nanocomposite properties. They concluded that nanotube waviness can significantly reduce the effective reinforcing modulus of the nanotubes, and thus limit the overall effective modulus of the reinforced polymer, as shown in Fig. 2.11(b) for a range of CNT volume fractions. The same model was employed by Bradshaw et al. [122], where it was used to compute the dilute strain concentration tensor. This tensor was in turn used in a micromechanical analysis to study the curvature effect on the effective elastic properties of aligned and randomly oriented nanocomposites. The results also showed that nanotube waviness results in a reduction of the effective modulus of the composite. Furthermore, the degree of reduction is dependent on the ratio of the sinusoidal wavelength to the nanotube diameter. As this wavelength ratio increased, the effective stiffness of a composite with randomly oriented wavy nanotubes converged to the result obtained with straight nanotube inclusions.

Figure 2.11 (a) A representative cell for the analysis of wavy nanotubes and (b) the detrimental effect of nanotube waviness of the effective Young’s modulus of a nanocomposite as determined from micromechanical methods (From Ref. [120]).

Chen et al. [123,124] developed an analytical model based on shear lag theory to study the effect of CNT curvature on the mechanical properties and pull-out response. The model accounted for the entire pull-out process, namely, the bonded, debonding and sliding stages. Two interface
friction models were applied. They showed that a Coulomb friction model can better account for the fiber curvature effect than a constant friction model. A parametric study showed that fibers with more curvature, longer embedded lengths, and higher friction interfaces with the surrounding matrix required additional pull-out force and energy for complete pull-out. Pantano et al. [125] also studied the effects of CNT waviness and interfacial bonding on the composite stiffness using micromechanical techniques. They recognized that in the case of weak interfacial bonding, CNT waviness can actually increase the stiffness of the composite. The transverse shear loads are transmitted to wavy CNTs through lateral normal interactions with the matrix. These transverse forces within the CNT generate locally varying bending moments along the CNTs. The strain energy associated with local bending of wavy MWCNTs, can thus provide a novel mechanism for enhancing polymer composite stiffness, even in the presence of weak interfacial bonding. Thostenson and Chou [126] used micromechanical techniques to investigate the elastic properties of short and aligned CNT polymer composites. They concluded that the nanocomposite elastic properties are particularly sensitive to the nanotube diameter, since larger-diameter nanotubes show a lower effective modulus and occupy a greater volume fraction in the composite relative to smaller diameter nanotubes.

Recently, an interfacial cohesive law has been developed by Jiang et al. and applied to study the interaction between CNT walls [127] and CNT polymer composites [128]. The cohesive law and its properties are obtained directly from the LJ potential. The cohesive law was used in a micromechanical analysis to predict the stress-strain behavior of CNT polyethylene composites [129]. 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.

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. [130]. 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 FE results.
2.3.3 Existing Multiscale Modeling Techniques

The mechanical deformation and failure of many engineering materials are in fact multiscale phenomena and the observed macro-scale behavior is governed by processes that occur on many different length and time scales. These processes are often dependant on each other and effect the overall deformation. It is therefore necessary to model these systems using a variety of length scales, which accurately represent the governing physics. Since various scales in the system depend on each other, it is essential to formulate it in terms of multiscale modeling, whereby the scales of interest are coupled or integrated into a unified approach. Clearly, the degree to which these scales are coupled would depend upon the system being investigated. Hence, varied multiscale approaches currently exist in the literature [131-135].

Most multiscale modeling techniques adopt either sequential or concurrent approaches to treat this class of problems where it is common to employ MD (or TB) for atomistics and finite element methods (FE) for continuum scales. The sequential approach assumes that the problem considered can be easily separated into processes that are governed by different length and time scales. In doing so, the simulations are running independently of each other and a complete separation of both length and time scales is achieved. The output (displacement or force fields) of the finer scale simulation are used as boundary conditions for the coarser scale. Since the simulations are not integrated, it is important to feedback the force fields for comparison to ensure that the simulations are converging. However, it should be noted that the uniqueness of the solution is still not guaranteed. A schematic of the sequential approach is given in Fig. 2.12.

Figure 2.12 Schematic of the sequential multiscale modeling approach.
Concurrent methods perform the entire multiscale simulation simultaneously and continually feed information from one length scale to the other in a dynamic fashion. Concurrent methods are better suited in representing scales with a strong dependence because of the continuous transfer of information between the different scales. The passing of information ensures consistency amongst the field variables between the two simulation methods. This two-way transfer of boundary conditions is achieved through the use of a transition region depicted in Fig. 2.13. Unfortunately, most concurrent multiscale modeling techniques suffer from one or more of the following difficulties: (i) the necessity of meshing traditional FE regions down to the atomic scale, thus leading to physical inconsistencies and numerical difficulties, (ii) contamination of the solution due to wave reflection resulting from the improper description of the transition zone and (iii) the FE/MD energy mismatch leads to erroneous non-physical effects in the transition region. A number of reviews detailing the different multiscale modeling techniques, their merits and limitations are provided in [136-138].

Namilae and Chandra [139] developed a sequential multiscale model linking MD and FE to study the effect of chemical functionalization of the interfacial properties. They used MD to simulate nanotube pull-out tests from which they obtained the corresponding traction separation curves describing the interface. They then used these results to evaluate cohesive zone model parameters in a FE framework. They predicted that an ISS as high as 5 GPa can be achieved through the chemical bonding of the CNT and matrix.
A sequential multiscale model was proposed by Odegard and co-workers in which the nanotube, polymer matrix, and interface were all combined and modeled by an effective continuum fiber [140,141]. The fiber was developed through the use of an equivalent-continuum modeling method. In this approach, MD was used to model the molecular interactions between the nanotube and polymer. Then micromechanical methods were employed to determine the bulk properties of the effective fiber embedded in a continuous polymer. Figure 2.14 illustrates how the molecular level description of the system is related to the continuum level with an intermediate truss model. The authors used this method to examine the effective properties of the nanocomposite. The elastic stiffness constants were determined for both aligned and randomly orientated nanotubes and for varied nanotube lengths and concentrations.

A hierarchical multiscale Monte Carlo finite element method (MCFEM) was developed by Spanos and Kontsos [142] to determine the mechanical properties of polymer nanocomposites. In their approach, special consideration was taken to account for the non-uniform spatial distribution of the CNTs in the polymer in an effort to closely replicate experimental results which are hindered by the inhomogeneous dispersion of the nanofillers. This method effectively divides the composite into a grid of material regions, similar to the RVE used in other techniques, each containing a material point. The material points are introduced to model variations in the volume fractions of the CNTs. The finite element method is used to discretize
the structure into a set of unit cells each with different homogenized properties. Here, the model uses the equivalent continuum technique developed by Odegard et al. to determine the material properties of the SWCNT as an input to a Mori-Tanaka micromechanical analysis which subsequently determines the averaged properties of each unit cell. The finite element method computes estimates for the overall mechanical behavior of the nanocomposite. Finally, a statistical analysis of the ensemble of the numerically generated results yields values for the Young’s modulus and Poisson ratio of the composite.

Li and Chou [143] are responsible for the development of a molecular structural mechanics approach which has been used extensively to model CNT based structures. In this approach, the CNT is modeled as a space frame structure, where the covalent C-C bonds are represented as beams joined together by nodes which represent the atom positions. The tensile resistance, flexural rigidity, and torsional stiffness of the beams are determined by imposing energy equivalence on the structural mechanic and molecular mechanic energy descriptions of the beam and bond deformation mechanisms. This provides a relationship between the structural mechanics parameters and molecular mechanics force fields from which it is possible to obtain linear relationships between the tensile and shear moduli of each beam and the harmonic force constants. Li and Chou further applied this technique to the development of an atomistic-based continuum model to study the compressive behavior of the bulk composite [144]. In this approach the nanotube was modeled by the molecular structural mechanics approach, the polymer matrix was modeled at the continuum scale by the finite element method, and the interface between the nanotube and polymer was represented by a truss rod model whereby the atomic interactions are based on the LJ potential. By use of this model the authors considered two cases of loading, isostress and isostrain conditions. For both loading conditions the model showed that the maximum shear stresses occurred at the nanotube ends and the shear stresses vanish at the middle section of the nanotube. They also concluded that the buckling force is dependent on the volume fraction of nanotube, and increases with increasing nanotube length.

The elastic properties of CNT polymer composites under various loading conditions were also studied through the development of a multiscale model by Hu et al. [145]. In this model a RVE was created which encompassed the nanotube, transition layer between nanotube and polymer matrix, and the outer polymer matrix body. An equivalent beam model of the nanotube was developed using a combination of molecular mechanics and structural mechanics approaches.
This way, a relationship between the material properties of the beam element and molecular mechanic force fields is obtained in a similar fashion to the study by Li and Chou [143]. In order to describe the interaction between the nanotube and polymer matrix, the authors used molecular mechanic and dynamic approaches to obtain the thickness of the transition layer or equilibrium distance between the nanotube and polymer. The transition layer and outer polymer matrix were modeled using the finite element method. In this study, no chemical bonding was assumed between the nanotube and polymer. In this case, the LJ potential was used to characterize the interaction between the nanotubes and polymer matrix. The authors used the model to study the effects of such parameters as volume fraction of nanotubes, stiffness of the transition layer, and length of the polymer chain on the elastic properties of the bulk composite composed of short unidirectional nanotubes.

2.4 The Need for the Current Studies

A number of theoretical and experimental efforts have been devoted to characterize the mechanical properties of CNT-based nanocomposites. It is difficult to generalize across these studies because of the large number of parameters that can influence the effective properties including the processing conditions, CNT-polymer interactions, the modeling techniques adopted and the specifics of the polymer chemistry. However, the literature indicates that there exist three key areas that need to be further explored and developed in order to fully harness the potential of CNT-based nanocomposites and their hypothesized applications. These are listed below and include; (i) CNT dispersion, (ii) load transfer across the CNT polymer interface, (iii) accurate models of nanocomposite behavior, and (iv) multifunctionality for self-health monitoring. The work presented in this thesis addresses these issues and further elucidates on the mechanics of CNT reinforced nanocomposites.

2.4.1 CNT Dispersion

Due to the significant variability in property measurements of CNT polymer composites, even for systems with the same constituent materials, it becomes evident that the dispersion process is of key importance. There are several techniques available to improve the dispersion of nanofillers into polymeric matrices but there is as of yet no simple and consistent method which can be applied without fail. Furthermore, the homogeneous dispersion of CNTs has only been achieved on a laboratory scale and to a limited concentration of approximately 1-5 wt%. Clearly,
much more research work needs to be done in this area. The literature indicates that techniques to disperse nanofillers in solutions invariably suffer from problems associated with the strong interactions between nanofillers and their tendency to agglomerate [146]. However, surface treatment methods, used in conjunction with mechanical shearing techniques, can potentially provide a means of counteracting these effects.

2.4.2 Interfacial Characteristics and Load Transfer

The mechanical properties of a composite material are governed by the characteristics of the reinforcing filler-polymer matrix interface. The interface is largely responsible for stress transfer from the surrounding matrix to the reinforcement. As such, the extremely high aspect ratios of CNTs lend themselves to greatly improved transferability of load at the interface, when compared with conventional microfibers. However, the degree of interfacial adhesion between the nanotubes and polymer also becomes a key parameter affecting the physical properties of the nano-reinforced composite. The carbon atoms on CNT walls are chemically stable because of the aromatic nature of the bonding. As a result, the reinforcing CNTs interact with the surrounding polymer matrix mainly through weak vdW interactions [145].

Studies suggest that it is possible to improve the interfacial strength between the CNTs and polymer matrix using chemical modification techniques. Experimental nanotube pull-out tests seem to support the idea that chemical modification can increase the interfacial shear strength (ISS) of CNT polymer composite systems. For example, the work by Wagner’s group has demonstrated that the ISS between a multiwalled carbon nanotube (MWCNT) and an epoxy matrix is in the range of 35 to 376 MPa using a scanning probe microscope (SPM) setup to drag the nanotube out from the matrix [100]. Later, they employed an atomic force microscope (AFM) to directly pull a MWCNT from a polyethylene-butene matrix and observed an average interfacial stress of 47 MPa [103]. Traditional composite materials containing microfiber reinforcements embedded in thermoplastic matrices typically exhibit interfacial strengths below 10 MPa [147]. Furthermore, computer simulations have shown that the interfacial strength of a CNT polyethylene system is on the order of 2 MPa, when only vdW interactions were considered [110]. Therefore, it can be concluded that some form of covalent bonding does naturally occur in the above system as evidenced by the high interfacial strength.
Evidently, a number of analytical, numerical and experimental works has been done to help understand the complexities of the CNT polymer interface. However, correlation between these results is often difficult due to (i) significant variability in the materials, processing techniques and procedures that are employed in experimental studies and (ii) differences in the adopted simulation techniques and the way the pull-out problem is formulated in the numerical investigations. Some conclusions drawn experimentally have not been observed in numerical and analytical simulations. Specifically, experimental results exhibit high pull-out forces at the initial stage of the pull-out process. This is immediately followed by a sudden decay in the force until the CNT has fully been withdrawn from the polymer. On the contrary, the pull-out forces predicted by numerical simulations seem to increase to a relatively fixed value until the last stages of the pull-out process. Therefore, several fundamental differences between experimental studies and numerical simulations are worthy of investigation.

2.4.3 Theoretical Models

Over the last several decades research in the area of composite materials has become quite mature. A number of well-established theories and numerical models have been developed as predictive tools in support of experimental efforts. However, in many cases it will be necessary to extend these theories, which have been developed for macroscale composites, to account for phenomena that are specific to the nanoscale. From the viewpoint of modeling, CNTs and their use as reinforcements in polymers are challenging because of the varied length scales involved. Discrete atomistic approaches such as MD are computationally prohibitive and to date have been limited to modeling only short nanotube segments. For the coarser scales, the fields of micromechanics and continuum mechanics are well established but not well-suited to model details at the atomistic level that are likely to be important for nanostructured materials. For these classes of materials it becomes necessary to formulate the problem in terms of multiscale modeling, whereby the scales of interest are coupled or integrated into a unified approach. Section 2.3.3 of this thesis summarized a number of multiscale efforts but the literature indicates that this field is still in its infancy.

2.4.4 Multifunctionality and Self-Health Monitoring

CNT polymer composites are beginning to show promise for a variety of applications in the aerospace industry where improvements in thermal, electrical and mechanical properties of structural materials are a key goal. In parallel, there is a growing demand for multifunctional
materials that provide continuous and integrated monitoring of damage phenomena in an efficient and cost affordable way. Unlike traditional structural systems, where only one material property is enhanced (e.g., strength/toughness), multifunctional systems are capable of fulfilling several design requirements (e.g., strength/toughness, condition monitoring, actuation, and power generation). The concept of multifunctional materials with sensing capabilities combined with enhanced mechanical-electrical and/or thermal properties could prove useful for the high requirements of the aerospace sector.

The engineering community is aggressively pursuing novel sensing technologies to enable automated damage detection of critical load bearing components/systems, known hereafter as structural health monitoring (SHM) [148-152]. By exploring the architecture and the interplay of the electrical and mechanical properties of a CNT network in a composite’s matrix, new nanoscale methodologies of SHM and internal damage sensing can be realized. The addition of CNTs in a polymer matrix significantly increases the electrical conductivity of the resulting composite through the formation of an electrically percolating network [153-155]. By passing an electric current through the composite and measuring its electrical resistance, it is possible to monitor the architecture of the CNT network and the strain fields in the material. It is for this reason that CNT polymer composites are being exploited in the field of SHM. By studying the electrical footprint of damage phenomena in composite materials using percolating CNT networks, an enhancement in the safety of composite usage and reduced maintenance of the composites can potentially be seen. These potential benefits have lead to an increased interest in researching CNT polymer composite SHM systems [156-159]. However, as of late, research in this field has been done to a small degree and only minor correlations between electrical resistance measurements and internal damage mechanisms have been made [156,157].
Chapter 3
Multiscale Modeling of Nanocomposites Using Atomistic-Based Continuum Method

Summary: In this chapter, we describe the ABC multiscale modeling technique in detail. Specifically, we describe how the modeling method is used to simulate CNTs of varied chiral indices and the CNT/epoxy matrix interface. The model is used to predict the constitutive response of CNTs and their fracture characteristics under both tensile and torsional loads. Furthermore, we describe the development of the RVE and provide a brief review of molecular dynamics and pertinent interatomic potentials and the finite element method.

3.1 Molecular Dynamics

Molecular dynamics is a computational method used to simulate the time dependent behavior of molecular systems. MD simulations provide a means of investigating the structure, dynamics, and thermodynamics of individual molecules. The simulations generate trajectories that describe the atomic positions, velocities, and accelerations of individual particles as they vary with time. These trajectories are then used to obtain average values of system properties such as energy, pressure and temperature.

At the core of the molecular dynamics method is the process of determining the forces acting on individual atoms. These forces are then used to evolve the simulations in time by incorporating them into Newton’s second law, as follows:

\[ \vec{F}_i = m_i \ddot{a}_i \]  

(1)

where \( \vec{F}_i \) is the force acting on particle \( i \), \( m_i \) is the mass of particle \( i \), and \( \ddot{a}_i \) is its acceleration. The atomic forces are determined by taking the gradient of the system’s total potential energy, as given by

\[ \vec{F}_i = -\nabla_i V(\vec{r}) \]  

(2)
where \( V(\vec{r}) \) is the system's position dependent interatomic potential. It represents the potential energy of the system when the atoms are arranged in a specific configuration. Combining equations (1) and (2)

\[
-\nabla_i V(\vec{r}) = m_i \vec{a}_i
\]

(3)

demonstrates that the derivative of the potential energy with respect to the particle position can be related to the acceleration of that particle.

Only the initial positions, velocities, and an expression for the total system potential energy need to be provided to conduct a MD simulation. In most MD simulations, the initial atomic positions are determined by the material and the problem being simulated, whereby they are chosen to coincide with the atomic lattice locations. The initial velocities are generated randomly based on statistical mechanics at a specified temperature. The other quantity of interest needed to conduct an MD simulation is an expression for the total potential energy. The total potential energy of an atomic system is described using classical interatomic potentials that can be expressed in a wide variety of forms. These potential functions become extremely complicated when accurately representing the atomic interactions. The nature of this complexity is due to quantum effects taking place at the subatomic level that are responsible for chemical properties such as valence and bond energy. Quantum effects are also responsible for the spatial arrangement (topology) of the interatomic bonds, their formation and breakage. In order to obtain reliable results in molecular dynamic simulations, the interatomic potential should accurately account for these quantum mechanical processes. The general expression for total atomistic potential energy can be expressed as

\[
V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \sum_i V_i(\vec{r}_i) + \sum_{i,j > i} V_{ij}(\vec{r}_i, \vec{r}_j) + \sum_{i,j,k > j > i} V_{ijk}(\vec{r}_i, \vec{r}_j, \vec{r}_k) + ... \tag{4}
\]

where \( N \) is the number of atoms in the system and \( \vec{r}_N \) is the radius vector of the Nth atom. The functions \( V_m \) are called \( m \)-body potentials and describe the interaction of one to \( m \) pairs of atoms. The first term represents the energy of the isolated atom \( i \) or equivalently, the energy due to an external force field, such as gravitational or electrostatic. The second accounts for pair-wise interactions of the atoms \( i \) and \( j \), and the third for the three-body interactions, and so on.
The reduction from a fully quantum description to a classical potential entails two main
approximations [160]. The first one is the Born–Oppenheimer approximation, which states that
the dynamics of electrons is so fast that they can be considered to react instantaneously to the
motion of their nuclei. As a consequence, they may be treated separately. The second one treats
the nuclei, which are much heavier than electrons, as point particles that follow classical
Newtonian dynamics. In molecular dynamics the effect of the electrons is approximated as a
single potential energy surface.

In the field of molecular dynamics, a number of different interatomic potentials have been used.
This is primarily because of the large variance in the material systems being studied. The choice
of potential for a molecular dynamics simulation is determined by factors such as the material
being modeled, the bond type, the desired accuracy, and available computational resources.
However, two main categories exist; two-body interatomic potentials and many-body potentials.

3.1.1 Two-body (pair) potentials

The potential functions representing the non-bonded energy of an atomic system are formulated
as a sum over interactions between the particles of the system. The simplest choice is the pair
potential, in which the total potential energy can be calculated from the sum of energy
contributions between pairs of atoms. At the subatomic level, the electrostatic field due to the
positively charged atomic nucleus is neutralized by the negatively charged electron clouds
surrounding the nucleus. Within the quantum mechanical description of electron motion, a
probabilistic approach is employed to evaluate the probability densities at which the electrons
can occupy particular spatial locations. The term ‘‘electron cloud’’ is typically used in relation to
spatial distributions of these densities. The negatively charged electron clouds, however,
experience cross-atomic attraction, which grows as the distance between the nuclei decreases. On
reaching some particular distance, which is referred to as the equilibrium bond length, this
attraction is equilibrated by the repulsive force due to the positively charged nuclei. A further
decrease in the inter nuclei distance results in a quick growth of the resultant repulsive force.

An example of such a pair potential is the Lennard–Jones potential, used for calculating van der
Waals forces. The LJ potential is written as:
where $\mu$ is the potential well depth, $\psi$ is the hard sphere radius of the atom or the distance at which $V_{LJ}$ is zero, and $r$ is the distance between the two atoms. The first term of this potential represents atomic repulsion, dominating at small separation distances, while the second term accounts for the attraction (bonding) between two atoms. The LJ potential is most widely used to model vdW interactions.

Another common pair potential is the Modified Morse potential. This potential is well suited for characterizing the behavior of C-C covalent bonding, and has been used by several authors in purely atomistic [53,161] simulations of CNT fracture and growth. This potential consists of two parts: a bond stretching component and an angle-bending component, as given by:

$$V_{MM} = V_s + V_b$$

$$V_s = D_e \left( 1 - \exp \left( -\beta (r-r_0) \right) \right)^2 - 1$$

$$V_b = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \left[ 1 + k_{\text{sextic}} (\theta - \theta_0)^4 \right]$$

where $r$ is the current bond length, $\theta$ is the current angle of the adjacent bond, $D_e$ is the dissociation energy, $\beta$ is a constant which controls the ‘width’ of the potential, and $k_\theta$ and $k_{\text{sextic}}$ are the angle-bending force constants. This is the usual form of the Morse potential except that the angle-bending component has been added and the parameters are slightly modified to correspond with the Brenner potential for strains below 10%. The reason for this being that the Brenner potential is considered more accurate and versatile due to its ability to account for bond hybridization and bonds with atoms other than carbon. Tserpes et al. [162] suggest that the angle-bending component can be neglected. However, this component has been found to contribute to the initial stability of the CNT. Without the addition of the angle-bending component, the CNT will experience unstable configuration and tends to collapse on itself as will be shown in Section 7.1.1 of this thesis.

In many-body potentials, the potential energy includes the effects of three or more particles interacting with each other. In simulations with pairwise potentials, global interactions in the
system also exist, but they occur only through pairwise terms. In many-body potentials, the potential energy cannot be found by a sum over pairs of atoms, as these interactions are calculated explicitly as a combination of higher-order terms.

### 3.1.2 Many-body Potentials

A key motivation for developers of many-body potentials is to enable more accurate modeling of specific classes of materials such as metals, ceramics, oxides, or CNTs. The challenge in many-body potentials is to know what physics and chemistry to include to capture the desired physical effects but also what can be excluded to enhance computational efficiency. In contrast to pairwise potentials, many-body potentials, as the name implies, explicitly include many-body effects. The energy expression for the potential is typically written as a sum over interactions that involve not just two, but clusters of three or more nearby atoms. The atoms participating in each interaction depend on their current configuration, so that covalent bonds can effectively break and form again as atoms move which is captured effectively by many-body potentials. Table 3-1 lists eight such many-body potentials, the year they were first published and the materials they are commonly used to model as taken from reference [163] while the following sections describe two such potentials used in this work.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Year</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Embedded-Atom Method (EAM)</td>
<td>1983</td>
<td>fcc metals</td>
</tr>
<tr>
<td>Modified Embedded-Atom Method (MEAM)</td>
<td>1987</td>
<td>metals</td>
</tr>
<tr>
<td>Tersoff</td>
<td>1988</td>
<td>covalent solids</td>
</tr>
<tr>
<td>Reactive Empirical Bond Order (REBO)</td>
<td>1990</td>
<td>CNTs</td>
</tr>
<tr>
<td>Bond–Order Potential (BOP)</td>
<td>1999</td>
<td>covalent solids</td>
</tr>
<tr>
<td>Adaptive Intermolecular REBO (AIREBO)</td>
<td>2000</td>
<td>multiwall CNTs</td>
</tr>
<tr>
<td>Reactive Force Field (ReaxFF)</td>
<td>2001</td>
<td>universal</td>
</tr>
<tr>
<td>Charge Optimized Many-Body (COMB)</td>
<td>2007</td>
<td>oxides</td>
</tr>
</tbody>
</table>
The Tersoff Interatomic Potential

The Tersoff potential [164] is a three-body potential function which explicitly includes an angular contribution of the force. The potential is widely used in various applications for silicon and carbon. It is written in the following form:

\[ V_{\text{Tersoff}} = \frac{1}{2} \sum_i \sum_{i \neq j} f_{\text{cut}}(r_{ij}) \left[ f_R(r_{ij}) + b_{ij} f_A(r_{ij}) \right] \]  

(9)

where \( f_{\text{cut}}(r_{ij}) \) is a smooth cut-off function and \( f_R(r_{ij}) \) and \( f_A(r_{ij}) \) are repulsive and attractive energy terms, respectively, and are given by:

\[ f_{\text{cut}}(r_{ij}) = \begin{cases} 1, & r_{ij} \leq R - D \\ \frac{1}{2} \left[ 1 - \frac{\sin \left( \frac{\pi (r_{ij} - R)}{2D} \right)}{\pi} \right], & R - D < r_{ij} \leq R + D \\ 0, & r_{ij} > R + D \end{cases} \]  

(10)

\[ f_R(r_{ij}) = A \exp(-\lambda_1 r_{ij}) \]  

(11)

\[ f_A(r_{ij}) = B \exp(-\lambda_2 r_{ij}) \]  

(12)

where \( A, B, \lambda_1 \) and \( \lambda_2 \) are parameters of the potential. The parameters \( R \) and \( D \) are chosen as to include the first-neighbor shell only for the selected structure (for carbon \( R=1.8A \)). The main feature of this potential is the presence of the bond-order term, \( b_{ij} \). The basic meaning of this term is that the strength of each bond depends on the local environment and is lower when the number of neighbors is relatively high. The bond-order term is defined as:

\[ b_{ij} = \frac{1}{(1 + \beta n_{ij}^{\phi_n})^{1/2n}} \]  

(13)

\[ \zeta_{ij} = \sum_{k \neq i,j} f_{\text{cut}}(r_{ij}) G(\theta_{ijk}) \exp\left[ \lambda_3^3 (r_{ij} - r_{ik})^3 \right] \]  

(14)

\[ G(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{(d^2 + (h - \cos \theta)^2)} \]  

(15)

where \( c, d, \) and \( h \) are parameters of the potential.
The AIREBO Interatomic Potential

The adaptive intermolecular REBO (AIREBO) potential [165] is an extension of the REBO potential with added LJ and torsional terms. The AIREBO potential is written as:

\[ V^{\text{AIREBO}} = V^{\text{REBO}} + V^{\text{LJ}} + V^{\text{Torsion}} \]  

(16)

The \( V^{\text{REBO}} \) term gives the AIREBO potential model its reactive capabilities and only describes short-ranged C-C, C-H and H-H interactions (\( r < 2 \) Angstroms). The \( V^{\text{LJ}} \) term adds longer-ranged interactions (\( 2 < r < \text{cutoff} \)) using the standard Lennard-Jones potential. The \( V^{\text{Torsion}} \) term is an explicit 4-body potential that describes various dihedral angle preferences in hydrocarbon configurations which is defined as

\[ V^{\text{Torsion}} = \frac{1}{2} \sum_i \sum_j \sum_k \sum_l \sum_{ijkl} w_{ij}(r_{ij}) w_{jk}(r_{jk}) w_{kl}(r_{kl}) V^{\text{Torsion}}(w_{ijkl}) \]  

(17)

where \( w_{ij}(r_{ij}) \), \( w_{jk}(r_{jk}) \) and \( w_{kl}(r_{kl}) \) are the bond-weight terms, \( V^{\text{Torsion}} \) is the torsional potential defined as a function of the dihedral angle \( w_{ijkl} \). More details can be found in reference [165].

The REBO potential function is based on Tersoff’s covalent-bonding formalism with additional terms that correct for an inherent over-binding of radicals and that include nonlocal effects [166]. The binding energy is given as a sum over bonds as

\[ V^{\text{REBO}} = \sum_i \sum_{j<i} \left[ V_R(r_{ij}) - B_{ij} V_A(r_{ij}) \right] \]  

(18)

where each contribution is expressed as

\[ V_R(r_{ij}) = f_{\text{cut}}(r_{ij}) D_{ij}^{(e)} \frac{1}{(S_{ij} - 1)} e^{-\frac{S_{ij}}{2} \rho_0 (r_r - r_r^{(e)})} \]  

(19)

\[ V_A(r_{ij}) = f_{\text{cut}}(r_{ij}) D_{ij}^{(e)} S_{ij} \frac{1}{(S_{ij} - 1)} e^{-\frac{S_{ij}}{2} \rho_0 (r_r - r_r^{(e)})} \]  

(20)

\( V_R \) and \( V_A \) are pair-additive repulsive and attractive interactions, respectively, and \( B_{ij} \) represents a many-body coupling between the bond from atom \( i \) to atom \( j \) and the local environment of atom \( i \). The function \( f_{\text{cut}}(r_{ij}) \) is a cut-off function which restricts the pair potential to nearest neighbors and is given by
\[
f_{\text{cut}}(r_{ij}) = \begin{cases} 
1, & r_{ij} < R_{ij}^{(1)} \\
1 + \cos \left( \frac{\pi (r_{ij} - R_{ij}^{(1)})}{R_{ij}^{(2)} - R_{ij}^{(1)}} \right) / 2, & R_{ij}^{(1)} < r_{ij} < R_{ij}^{(2)} \\
0, & r_{ij} > R_{ij}^{(2)} 
\end{cases}
\] (21)

where \( D_{ij}^{(e)} \) is the well depth, \( R_{ij}^{(e)} \) is the equilibrium distance and \( \beta_{ij} \) is the empirical bond-order function as given by

\[
\overline{B}_{ij} = \frac{B_{ij} + B_{ji}}{2} + F_{ij}(N_{ij}^{(t)}, N_{ji}^{(t)}, N_{ij}^{\text{conj}})
\] (22)

where

\[
B_{ij} = \left( 1 + \sum_{k(i,j)} G_i(\theta_{ijk}) f_{ik}(r_{ik}) e^{-\alpha \left[ (r_{ij} - R_{ij}^{(1)}) - (r_{ik}^{(1)}) \right]} + H_{ij}(N_{ij}^{(t)}, N_{ij}^{(c)}) \right)^{-\delta_i}
\] (23)

The quantities \( N_{ij}^{(H)} \) and \( N_{ij}^{(I)} \) are the number of carbon and hydrogen atoms respectively, bonded to atom \( i \), \( N_{ij}^{(t)} \) is the total number of neighbors (\( N_{ij}^{(H)} + N_{ij}^{(I)} \)) of atom \( i \) and \( N_{ij}^{\text{conj}} \) depends on whether a bond between carbon atom \( i \) and \( j \) is part of a conjugated system, \( G_i(\theta_{ijk}) \) is a function of the angle between bonds \( i-j \) and \( i-k \). The functions \( H_{ij} \) and \( F_{ij} \) are used for C-C and H-H bonds only and account for different atomic environments. All the constants for equations (19) – (23) are provided in [166].

3.1.3 Time Stepping

The total potential energy is a function of the atomic positions of all the atoms in the system. Due to the complexity of such a function, the resulting equations of motion are integrated numerically. Different numerical algorithms have been employed in MD simulations for integrating the equations of motion. The most popular of which is the Verlet algorithm [167]. All the algorithms assume that the positions, velocities and accelerations can be approximated by a Taylor series expansion as given by
\[ r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2} a(t)\Delta t^2 + \ldots \] (24)

\[ v(t + \Delta t) = v(t) + a(t)\Delta t + \frac{1}{2} \frac{d^3 r(t)}{dt^3} \Delta t^2 + \ldots \] (25)

and a similar expression for the acceleration. In the above \( \Delta t \) is the timestep used throughout the simulation. The verlet algorithm proceeds by only writing two third-order Taylor series expansions of the position, one forward in time and the other backward in time as follows:

\[ r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2} a(t)\Delta t^2 + \frac{1}{6} \left[ \frac{d^3 r(t)}{dt^3} \right] \Delta t^3 \] (26)

\[ r(t - \Delta t) = r(t) - v(t)\Delta t + \frac{1}{2} a(t)\Delta t^2 - \frac{1}{6} \left[ \frac{d^3 r(t)}{dt^3} \right] \Delta t^3 \] (27)

Then by combining the above two equations, we obtain

\[ r(t + \Delta t) = 2r(t) - r(t - \Delta t) + a(t)\Delta t^2 \] (28)

where \( a(t) \) is expressed as the force divided by the mass, and the force itself is a function of the positions as given by Eq. (2). This is the general form of the verlet algorithm. This method is time-reversible, has good energy conservation properties and has low memory storage because the velocities are not included in the time integration. However, removing the velocity from the integration introduces numerical inaccuracies. This has lead to the development of other algorithms that are based off of the Verlet method, namely the velocity Verlet [168] and Verlet leap-frog [169] algorithms which explicitly involve the velocity in the time evolution of the atomic coordinates. We refer the reader to three excellent reviews that address the molecular dynamics method in its entirety that have been published by Rafii-Tabar [170], Carlsson [171], and Ercolessi [172] for further reading.
3.2 The Finite Element Method

The traditional framework in mechanics has always been the continuum. Under this framework, materials are assumed to be composed of a divisible continuous medium, with a constitutive relation that remains the same for a wide range of system sizes. Continuum equations are typically in the form of deterministic or stochastic partial differential equations (PDE’s). The underlying atomic structure of matter is neglected altogether and is replaced with a continuous and differentiable mass density. Similar replacements are made for other physical quantities such as energy and momentum. Differential equations are then formulated from basic physical principles, such as the conservation of energy or momentum. There are a large variety of numerical methods that can be used for solving continuum partial differential equations, the most popular being FEM.

The finite element method is a numerical method for approximating a solution to a system of partial differential equations. The FEM proceeds by dividing the continuum into a number of elements, each connected to the next by nodes. This discretization process converts the PDE’s into a set of coupled ordinary equations that are solved at the nodes of the FE mesh and interpolated throughout the interior of the elements using shape functions. The main advantages of the FEM are its flexibility in geometry, refinement, and loading conditions.

The total potential energy under the FE framework consists of two parts, the internal energy $U$ and external work $W$

$$\Pi = U - W \tag{29}$$

The internal energy is the strain energy caused by deformation of the body and can be written as

$$U = \frac{1}{2} \int_{\Omega} \{\varepsilon\}^T [D] \{\varepsilon\} d\Omega \tag{30}$$

where $\{\sigma\} = \{\sigma_x, \sigma_y, \sigma_z, \tau_{xy}, \tau_{yz}, \tau_{xz}\}^T$ denotes the stress vector, $\{\varepsilon\} = \{\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, \gamma_{xy}, \gamma_{yz}, \gamma_{xz}\}^T$ denotes the strain vector, $[D]$ is the elasticity matrix, and $\Omega$ indicates that integration is over the entire domain. The external work can be written as
\[ W = \int_{\Omega} \{u \ v \ w\} \begin{bmatrix} F_x \\ F_y \\ F_z \end{bmatrix} d\Omega + \int_{\Gamma} \{u \ v \ w\} \begin{bmatrix} T_x \\ T_y \\ T_z \end{bmatrix} d\Gamma \]  

(31)

where \( u, v, \) and \( w \) represent the displacements in \( x, y, z \) directions, respectively, \( \{F\} \) is the force vector which contains both applied and body forces, \( \{T\} \) is the surface traction vector, and \( \Gamma \) indicates that the integration of the traction occurs only over the surface of the body. After discretization of the region into a number of elements, point-wise discretization of the displacements \( u, v, \) and \( w \) for the respective \( x, y, \) and \( z \) directions, is achieved using shape functions \([N]\) for each element, such that the total potential energy becomes

\[ \Pi = \frac{1}{2} \{d\}^T \int_{\Omega} [B]^T [D] [B] \{d\} d\Omega - \{d\}^T \int_{\Omega} \begin{bmatrix} F_x \\ F_y \\ F_z \end{bmatrix} d\Omega - \{d\}^T \int_{\Gamma} \begin{bmatrix} T_x \\ T_y \\ T_z \end{bmatrix} d\Gamma \]  

(32)

where \([B]\) is the matrix containing the derivatives of the shape functions, and \( \{d\} \) is the displacement vector. With an expression for the total potential energy of the system in hand, one applies the principle of minimum potential energy to obtain the systems equilibrium configuration. The minimization of the total potential energy provides a solution that is compatible and equilibrated such that the displacement field satisfies the boundary conditions and interelemental continuity. A full description of the finite element method can be found in either of the texts by Hughes [173] or Zienkiewicz [174].

### 3.3 Representative Volume Element

A three-dimensional nonlinear RVE is developed to study the nano-reinforced epoxy system. The RVE consists of the reinforcing CNT, the surrounding polymer matrix, and the CNT-epoxy interface, as depicted in Fig. 3.1. 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 vdW interactions between the atoms in the CNT and the atoms in the epoxy matrix are described using the LJ interatomic potential. This description implies the assumption of a non-bonded interfacial region. A detailed description of all the components used in the development of the RVE is presented below.
3.3.1 Atomistic-based Continuum Representation of CNT Structures

In this study, two distinct CNT structures are investigated: the (16,0) zigzag nanotube and the (9,9) armchair nanotube, each having an approximate diameter of 1.2 nm. 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. 3.2. 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. Consequently, the terms node and atom are used interchangeably throughout this thesis. We adopt the Modified Morse interatomic pair potential with an added angle-bending term (Eq. (6)) to describe the atomic interactions in the CNT and to develop material models for the continuum elements. The parameters used for the potential in this study are the same as those adopted by Belytschko et al. [161], and are presented in Table 3-2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_o ) (m)</td>
<td>1.421 x 10^{-10}</td>
<td>( \theta_o ) (rad)</td>
<td>2.094</td>
</tr>
<tr>
<td>( D_e ) (N m)</td>
<td>6.03105 x 10^{-19}</td>
<td>( k_0 ) (N m rad^{-2})</td>
<td>0.876 x 10^{-18}</td>
</tr>
<tr>
<td>( B ) (m^{-1})</td>
<td>2.625 x 10^{10}</td>
<td>( k_{\text{sextic}} ) (rad^{4})</td>
<td>0.754</td>
</tr>
</tbody>
</table>
Figure 3.2 Carbon nanotube space-frame structure and beam element connectivity.

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, as depicted in Fig. 3.3. 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.7) with respect to the change in bond length and by utilizing the following relationship,

\[ \varepsilon = \left( r - r_0 \right) / r \],

we can arrive at the expression:

\[ F = 2 \beta D_c \left( 1 - \exp^{-\beta \varepsilon} \right) \exp^{-\beta \varepsilon} \quad (33) \]

which represents the force required to stretch a C-C bond. The interlayer spacing of carbon nanotube walls is assumed to be 0.34 nm and is also widely regarded as the CNT wall thickness [30-33]. This implies that the diameter of each bond or beam element is also 0.34 nm. The corresponding cross-sectional area is 0.09079 nm\(^2\). Utilizing this area and the above expression in Eq. (33), we are able to derive the stress-strain relationship (Fig. 3.4) for the beam elements. The initial stiffness of the beam elements is calculated to be 1.3 TPa.
Similarly, recognizing that the derivative of the angle-bending component of the potential with respect to the change in rotation is equivalent to the moment required to bend neighboring bonds, we arrive at the following expression:

\[
M = k_\theta \Delta \theta \left[1 + 3k_{\text{sextic}} (\Delta \theta)^2\right]
\]  

(34)

The moment/rotation curve obtained from Eq. (34) is shown in Fig. 3.5. Again, this curve is used to define the stiffness of the rotational spring elements throughout the simulation. The initial stiffness is calculated to be $8.76 \times 10^{-10}$ N nm rad$^{-2}$.

![Figure 3.3 Coincident node locations in rotational spring element definition.](image)

![Figure 3.4 The constitutive response of the beam elements as derived from the Modified Morse potential.](image)

Given the appropriate set of interatomic potentials and corresponding parameters, the other bond deformation mechanisms can also be included, i.e. dihedral angle torsion, out-of-plane torsion, van der Walls interactions and electrostatic interactions. However, several authors [30,175,176]
have stated that these effects are negligible and play an insignificant role in the simulation of nano-structured materials.

![Graph](image)

Figure 3.5 Constitutive response of the rotational spring elements as derived from the Modified Morse potential.

### 3.3.2 Atomistic-based Continuum Representation of Interfaces

Of importance to the development of an accurate and viable RVE is the appropriate representation of the interface between the CNT and the surrounding epoxy matrix. Different approaches can be adopted in characterizing the mechanisms and magnitudes of load transfer between a nanotube and the polymer matrix. The interfacial characteristics between CNTs and epoxy matrices remain unclear and researchers have reported a large range of interfacial shear stresses. However, it has recently been shown that the carbon atoms on CNT walls are chemically stable because of the aromatic nature of the bonding. As a result, the reinforcing CNTs interact with the surrounding matrix mainly through weak vdW interactions [145]. However, chemical functionalization techniques have been shown to drastically modify the interface via strong covalent bond formation, a process known as crosslinking. Therefore, as a preliminary basis, a non-bonded configuration is considered where only vdW interactions are assumed to exist. Upon examining the non-bonded interfacial properties of CNT/epoxy nanocomposites the interfacial description is modified to include strong covalent bonds via the Modified Morse potential as a means of strengthening the interface.
Due to its simplicity and sole dependence on the atomic separation distance, vdW interactions have most commonly been described using the LJ pair potential (Eq. (5)). In this thesis, we investigate the non-bonded interactions between the carbon atoms in the CNT and the atoms in the polymer. The parameters for these interactions are presented in Table 3-3.

<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>

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. 3.6. This approach is used in the small displacement static analyses of Section 5.2 where the linear elastic properties of the RVE are evaluated for homogenization purposes and compatibility with micromechanical modeling. Again, by differentiating the potential with respect to the separation distance, we arrive at an expression for the vdW force between two interacting atoms

$$F_{LJ} = 24 \left( \frac{\mu}{\psi} \right) \left[ 2 \left( \frac{\psi}{\gamma} \right)^{13} - \left( \frac{\psi}{\gamma} \right)^{7} \right]$$

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. By assuming that the truss rods share the same diameter as the beam elements described in the previous section, we can derive the constitutive relationship for each truss rod (Fig. 3.7). Here, the relationship extends to the usual LJ cut-off distance of $2.5\psi$ or 0.85 nm and the Poisson’s ratio for the truss rods is assumed to be 0.3.
A number of approaches have been considered to account for the interfacial properties of CNT reinforced composites. These depend on the type of bonding, type of polymer matrix, and load transfer mechanisms. Hence, the interfacial thickness has not yet been unambiguously defined. Several different values have been used in both atomistic and continuum simulations. Hu et al. [145] simulated the helical wrapping of one polystyrene chain around a CNT considering only vdW interactions via molecular dynamics. The equilibrium distance between the hydrogen atoms in the polymer and carbon atoms in the nanotube ranged from 0.2851 to 0.5445 nm. However, only one polymer chain was considered when in practical cases there may be other chains which also wrap around the nanotube. In comparison, Li and Chou [144] studied the compressive behavior of CNT/polymer composites and assumed that the inside surface of the polymer matrix
was located at the same position as the outside surface of the nanotube giving an interfacial thickness equal to 0.17 nm or half the thickness of the nanotube itself. Given the above variance, it is reasonable to assume an interfacial thickness of 0.3816 nm in our studies. Given that this value corresponds to the equilibrium distance of the LJ potential, the stable configuration of the nanotube and polymer matrix corresponds to a state of zero tensile or compressive stresses in the interfacial region. However, the effect of the thickness on the interfacial properties is investigated in Section 7.1.3 of this thesis. This same value was used by Montazeri and Naghdabadi [178] in their molecular structural mechanics model of SWCNT-polymer composites.

3.3.3 Homogenized Epoxy Matrix Representation

To model the surrounding epoxy matrix, a specific two-component epoxy structural adhesive is used based on a DGEBA / 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 details of these tests and the properties of the said adhesive are given in Section 6.2.1 of this thesis. The measured stress-strain response is input as multi-linear elastic material property in the present model and is depicted in Fig. 3.8. 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, 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-phenylenevinylene (PmPV), 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 [179]. Therefore, to avoid the computational limitations of MD, the atomic

![Figure 3.8 Constitutive response of epoxy polymer as determined from dogbone tension tests.](image-url)
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. 3.9, 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_{23.7}H_{27}O_{4.5}. The density of the resin is 1.16 g/cm³. The atomic structure of the curing agent is depicted in Fig. 3.10. It has a corresponding molecular mass of 146.23 g/mol, with a molecular formula of C_6H_{18}N_4 and a density of 0.93 g/cm³. 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/cm³, with an average polymer chain composed of C_{21.67}H_{26}O_{4.05}N. This corresponds to an average polymer chain mass of 356.01 u (atomic mass units), or 5.912 x 10^{-22} g. From this, a molecular density of 1.843 x 10^{21} molecules/cm³, or 1.843 molecules/nm³, 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 3-4. From this, we can infer an approximate polymer nodal density of 99 nodes/nm³ which defines the nodal refinement level in the polymer region for the varied volumes considered.

![Figure 3.9 Atomic structure of epoxy base resin.](image)

![Figure 3.10 Atomic structure of epoxy hardening agent.](image)
Table 3-4 Atoms present in the surrounding matrix per cubic nanometer.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atoms/nm³</th>
<th>% of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>38.41</td>
<td>39 %</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>51.79</td>
<td>52 %</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>6.47</td>
<td>6 %</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>2.88</td>
<td>3 %</td>
</tr>
</tbody>
</table>

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.

3.3.4 Assembled RVE

With all the components of the RVE defined and their constitutive laws established, the RVE can be constructed by combining the individual entities. Figure 3.11 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. 3.11 apart from the inset.
Chapter 4
Interfacial Characterization of Nano-Reinforced Adhesives Using Atomistic-Based Continuum

Summary: In this chapter, we describe the steps taken to characterize the CNT-epoxy interface using the ABC interface model. Specifically, we describe how the modeling method is used to simulate a nanotube pull-out experiment. The model is used to predict the pull-out profiles for the different cases considered and provide insight into the effects of such parameters as the CNT embedded length, the number of vdw interactions considered, the thickness of the interface, the morphology of the polymer, interfacial modification via chemical bond formation and the cut-off distance of the LJ potential.

4.1 Nanotube Pull-out

To investigate the interfacial properties of a CNT-polymer composite system, a pull-out test of the nanotube is simulated. Fiber pull-out tests have been well recognized as the standard method for evaluating the interfacial bonding properties of composite materials [180]. The problem is formulated using an RVE which consists of the reinforcing CNT, the surrounding polymer matrix, and the CNT/polymer interface as depicted in Fig. 4.1(a). Figure 4.1(b) shows a schematic of the pull-out process, where \( x \) is the pull-out distance and \( L \) is the embedded length of the nanotube. The CNT is modeled as described in Section 3.3.1 and the following sections describe the modifications made to the modeling of the interfacial and surrounding polymer regions.

![Figure 4.1 Schematic depictions of (a) the representative volume element and (b) the pull-out process.](image)
4.2 Interfacial Representation

The ABC approach presented in the previous chapter leads to a drastic increase in the number of degrees of freedom and the computational cost when conducting large displacement analyses. For example, each carbon atom in the CNT is involved in a large number of vdW interactions with the atoms in its surroundings. For example, there exist 3,379,744 vdW interactions across the interface for a nanotube of length 6.60 nm when no LJ cut-off distance is considered. Furthermore, the simulation environment poses a number of restrictions relating to pre-strain effects which need to be implemented in order to model the mechanics of the interface correctly. To overcome these limitations, a modified ABC approach is adopted in the modeling of the interface region and surrounding polymer for the large displacement pull-out simulations presented in Section 7.1.3.

In the modified ABC approach, the RVE is modified so as not to include any additional elements across the interface. Alternatively, the cumulative effect of the interactions acting on each CNT atom is applied as a resultant force on the respective node which is then resolved into its three Cartesian components. This process is depicted in Fig. 4.2. During each iteration of the pull-out process, the expression in Eq. 24 is re-evaluated for each vdW interaction and the cumulative resultant force and its three Cartesian components are updated to correspond to the latest pull-out configuration. Figure 4.3 shows a segment of the CNT with the cumulative resultant vdW force vectors as they are applied to the CNT atoms. This approach is also adopted to investigate the effect of interfacial modification via chemical bond formation as a means of strengthening the interface. However, in this case, the Modified Morse potential provided in Eq. 21 is used to simulate the covalent bonds across the interface.

![Diagram](image.png)

Figure 4.2 The process of nodal vdW force application. (a) vdW interactions on an individual CNT atom, (b) the cumulative resultant vdW force, and (c) the cumulative vdW Cartesian components.
4.3 Epoxy Matrix Representation

In the present study, we consider both a generic thermoset polymer and a specific two-component epoxy system. The generic polymer system will allow for us to identify the effect of polymer morphology and atomic density in the region surrounding a CNT on the ISS. Variations in polymer morphology and atomic density can also be interpreted as a means of investigating the effect of the number of vdW interactions considered. In this case, the polymer atoms involved in the vdW interactions at the interface are modeled as rings of nodes forming concentric cylinders around the CNT space-frame structure as depicted in Fig. 4.4. This approach adopts ordered and uniformly distributed representative nodes of the polymer structure. We feel that this description forms an adequate basis on which the interfacial properties of a generic polymer CNT system can be investigated. The density of nodes in the polymer description will determine the number of vdW interactions between the CNT and the surrounding polymer, and consequently, the resulting ISS. To study the sensitivity of this parameter on the ISS, the number of nodes in the polymer representation is varied.

In the case of the two-component epoxy system, we adopt the stoichiometric approach outlined in Section 3.3.3 to determine the approximate polymer nodal density. Here, the representative nodes are randomly distributed throughout a constant volume surrounding the CNT. We feel that this approach will provide a much more realistic depiction of the polymer and allows for us to predict the ISS for a specific CNT polymer system. We adopt a constant volume of polymer surrounding the CNT that extends a radial distance of 1.00 nm from the wall of the CNT. The model also utilizes an interfacial thickness of 0.38 nm and a CNT of 6.60 nm in length. The
surrounding polymer has a volume of 35.49 nm$^3$ which corresponds to a total of 3407 polymer nodes and a total of 3,379,744 vdW interactions occurring during the pull-out process. The polymer nodes are randomly distributed throughout this volume. In this way, the polymer representation closely mimics that of a true polymer system whereby the polymer chains adopt a random configuration. Figure 4.5 depicts the CNT embedded in the random two-component epoxy system and the distribution of polymer nodes. In both cases we consider the vdW interactions between the nanotube and the inner surface of the polymer matrix as well as those which extend further into the immediate surrounding matrix.

Figure 4.4 Polymer representation and pull-out boundary conditions.

Figure 4.5 CNT embedded in random polymer nodal distribution.
It is expected that cured thermoset polymer systems of a highly cross-linked formulation would show little deformation in the region surrounding a nanotube during a pull-out experiment [181]. Therefore, the representative nodes of the polymer are fully constrained and primarily serve to provide the coordinates of the polymer atoms involved in the vdW force evaluation procedure described above. The nodes in the CNT are constrained 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 displacement boundary conditions are summarized in Fig. 4.4.
Chapter 5
Micromechanical Determination of Effective Mechanical Properties of Nanocomposites

Summary: In this chapter, 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 Monte-Carlo FEA simulations used to predict the full constitutive response of the bulk nanocomposite subject to mechanical loading.

5.1 The Representative Fiber

In Section 4.3 of this thesis, we 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 [182,183]. 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. A general schematic of the approach is provided in Fig. 5.1.

![Schematic diagram of the proposed approach to scale-up to the macrolevel.](image)

**Figure 5.1 Schematic diagram of the proposed approach to scale-up to the macrolevel.**

### 5.1.1 Representative Fiber Constitutive Model

The constitutive relationship of the transversely isotropic representative fiber is:

\[
\sigma_{ij} = C^f_{ijkl} \varepsilon_{kl}
\]  

(36)

where \( \sigma_{ij} \) and \( \varepsilon_{kl} \) are the stress and strain components, respectively (\( i,j = 1,2,3 \)), and \( C^f_{ijkl} \) are the elastic stiffness components of the representative fiber (denoted by subscript \( f \)). Alternatively, Eq. (36) can be simplified by using the usual contracted notation for the elastic stiffness components and transversely-isotropic symmetry:

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} =
\begin{bmatrix}
C^f_{11} & C^f_{12} & C^f_{13} & 0 & 0 & 0 \\
C^f_{12} & C^f_{22} & C^f_{23} & 0 & 0 & 0 \\
C^f_{13} & C^f_{23} & C^f_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{(C^f_{22} - C^f_{23})}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & C^f_{66} & 0 \\
0 & 0 & 0 & 0 & 0 & C^f_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{bmatrix}
\]  

(37)

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, \( E^f_L \), longitudinal
shear modulus, $G'_L$, transverse shear modulus, $G'_T$, the plain-strain bulk modulus, $K'_T$, and the elastic stiffness component, $C_{ij}$. The elastic constants are related to the elastic stiffness components by:

\[
E'_L = C'_{11} = \frac{2C_{12}^f}{(C_{22}^f + C_{23}^f)} \\
G'_L = C'_{66} \\
G'_T = \frac{1}{2}(C_{22}^f - C_{23}^f) \\
K'_T = \frac{1}{2}(C_{22}^f + C_{23}^f)
\]

(38)

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.

### 5.1.2 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:

\[
u_i(B) = \varepsilon_{g}, x_j \\
T_i(B) = \sigma_{g}, n_j
\]

(39)

where $B$ is the bounding surface, $x_j$ is defined in Fig. 5.2 and $n_j$ are the components of the outward normal vector to $B$. The generalized total strain energy of the representative fiber is:

\[
\chi = \frac{V}{2} \sigma_{g}, \varepsilon_{ij} = \frac{\pi D^2 L}{8} \sigma_{g}, \varepsilon_{ij}
\]

(40)

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 $x_1$ 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. (39), the boundary conditions are:

$$
\begin{align*}
 u_i (B) &= e x_i \\
 T_2 (B) &= 0 \\
 T_3 (B) &= 0
\end{align*}
$$

(41)

The strain energy is:

$$
\chi = \frac{1}{8} \pi D^2 L E^f \epsilon^2
$$

(42)

The representative fiber strain energy, $\chi^f$, is equated to the strain energy of the RVE subjected to the boundary conditions in Eq. (41). 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. (42). The boundary conditions and strain energies for each of the five independent elastic properties are summarized and listed in Table 5-1. Unspecified strain components are zero valued.
Table 5-1 Elastic Constants and corresponding boundary conditions.

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Strain Energy Equation</th>
<th>Boundary Condition</th>
<th>Boundary Displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_L^f$</td>
<td>$\chi = \frac{1}{8}\pi D^2 L E_L^f e^2$</td>
<td>$\epsilon_{11} = e$</td>
<td>$u_1(B) = ex_i$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{22} = \sigma_{33} = 0$</td>
<td>$T_2(B) = 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T_3(B) = 0$</td>
</tr>
<tr>
<td>$G_L^f$</td>
<td>$\chi = \frac{1}{8}\pi D^2 L G_L^f e^2$</td>
<td>$\epsilon_{12} = e/2$</td>
<td>$u_1(B) = \frac{e}{2}x_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_2(B) = \frac{e}{2}x_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_3(B) = 0$</td>
</tr>
<tr>
<td>$G_T^f$</td>
<td>$\chi = \frac{1}{8}\pi D^2 L G_T^f e^2$</td>
<td>$\epsilon_{23} = e/2$</td>
<td>$u_1(B) = 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_2(B) = \frac{e}{2}x_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_3(B) = \frac{e}{2}x_2$</td>
</tr>
<tr>
<td>$K_T^f$</td>
<td>$\chi = \frac{1}{2}\pi D^2 L K_T^f e^2$</td>
<td>$\epsilon_{22} = \epsilon_{33} = e$</td>
<td>$u_1(B) = 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_2(B) = ex_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_3(B) = ex_3$</td>
</tr>
<tr>
<td>$C_{11}^f$</td>
<td>$\chi = \frac{1}{8}\pi D^2 L C_{11}^f e^2$</td>
<td>$\epsilon_{11} = e$</td>
<td>$u_1(B) = ex_i$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_2(B) = 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$u_3(B) = 0$</td>
</tr>
</tbody>
</table>

5.1.3 Material Property Summary

The five independent elastic constants and the resulting stiffness components, from Eq. (38), were determined for a representative fiber and RVE having a diameter, $D$, of 2.4 nm, a length, $L$, of 3.45 nm, and an applied strain, $e$, of 0.1%. These values are listed in Table 5-2 and the resulting constitutive law for the transversely isotropic representative fiber is given in Eq. (48) while that of the isotropic epoxy matrix is given in Eq. (49) using the values of 1.07 GPa and 0.3 for the epoxy’s Young’s modulus and Poisson ratio, respectively:
\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} = \begin{bmatrix}
469.3 & 7.3 & 7.3 & 0 & 0 & 0 \\
7.3 & 21.5 & 7.0 & 0 & 0 & 0 \\
7.3 & 7.0 & 21.5 & 0 & 0 & 0 \\
0 & 0 & 0 & 7.3 & 0 & 0 \\
0 & 0 & 0 & 0 & 26.0 & 0 \\
0 & 0 & 0 & 0 & 0 & 26.0
\end{bmatrix} \begin{bmatrix}
\epsilon_{11} \\
\epsilon_{22} \\
\epsilon_{33} \\
\epsilon_{23} \\
\epsilon_{13} \\
\epsilon_{12}
\end{bmatrix}
\]

(48)

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} = \begin{bmatrix}
2.02 & 0.87 & 0.87 & 0 & 0 & 0 \\
0.87 & 2.02 & 0.87 & 0 & 0 & 0 \\
0.87 & 0.87 & 2.02 & 0 & 0 & 0 \\
0 & 0 & 0 & 0.58 & 0 & 0 \\
0 & 0 & 0 & 0 & 0.58 & 0 \\
0 & 0 & 0 & 0 & 0 & 0.58
\end{bmatrix} \begin{bmatrix}
\epsilon_{11} \\
\epsilon_{22} \\
\epsilon_{33} \\
\epsilon_{23} \\
\epsilon_{13} \\
\epsilon_{12}
\end{bmatrix}
\]

(49)

Table 5-2 Representative fiber independent constants and elastic stiffness components.

<table>
<thead>
<tr>
<th>Elastic Constants</th>
<th>Value (GPa)</th>
<th>Stiffness Components</th>
<th>Value (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_T$</td>
<td>7.2</td>
<td>$C_{11}$</td>
<td>469.3</td>
</tr>
<tr>
<td>$K_T$</td>
<td>14.3</td>
<td>$C_{12}$</td>
<td>7.3</td>
</tr>
<tr>
<td>$G_L$</td>
<td>26.0</td>
<td>$C_{22}$</td>
<td>21.5</td>
</tr>
<tr>
<td>$E_L$</td>
<td>465.6</td>
<td>$C_{33}$</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_{66}$</td>
<td>26.0</td>
</tr>
</tbody>
</table>

5.2 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. (48) and (49). 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 [184] 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 [185]. Furthermore, a number of analytical efforts have employed the scheme in the prediction of the effective properties of various nanocomposites [186-188]. 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. For the following derivation, the term inclusion is at times used to refer to the CNT phase and we first consider the case where the CNTs are unidirectionally aligned within the matrix. Once the necessary parameters have been determined for this case, appropriate tensor transformations and volume averaging procedures will be introduced to account for the different nanotube orientations.

5.2.1 Mori-Tanaka Method for Unidirectionally Aligned CNTs

We assume that the composite is comprised of two-phases; the matrix will be denoted as phase $0$ with a corresponding stiffness $C_0$ and volume fraction $v_0$, while the CNT inclusion phase has a stiffness of $C_f$ and a volume fraction $v_f$. The matrix phase is assumed to be linearly elastic and isotropic, and perfect bonding between the CNTs and the matrix is assumed. The CNTs are further assumed to be ellipsoidal with a circular cross-section ($a_1=a_2$), an aspect ratio $\alpha_r$ (ratio of length to diameter), and aligned along the 1-axis (as shown in Fig. 5.3).

Figure 5.3 Schematic of the Mori-Tanaka method. (left) Two-phase composite material. (right) Comparison material.
Consider the two models shown in Fig. 5.3, representing the composite model and a “comparison material” with properties identical to those of the matrix. Displacements are now prescribed on the boundary of each material to give rise to a uniform strain $\varepsilon_a$ in each material. The stresses required to produce this uniform strain in each material are:

$$\bar{\sigma} = C_a \varepsilon_a, \quad \sigma_o = C_o \varepsilon_a$$

(50)

where $\bar{\sigma}$ and $\sigma_o$ are the average stress of the composite and comparison materials, respectively.

The strain field within the matrix material of the composite will not be uniform due to the presence of the nanotubes (and hence the average matrix strain $\bar{\varepsilon}_o$ will not equal $\varepsilon_a$), but rather will be perturbed by an amount $\bar{\varepsilon}_o^{pt}$ such that

$$\bar{\varepsilon}_o = \varepsilon_a + \bar{\varepsilon}_o^{pt}$$

(51)

where an overscore represents the volume average of the stated quantity. The average strain in the CNT phase is further perturbed from the of the matrix,

$$\bar{\varepsilon}_f = \bar{\varepsilon}_o + \varepsilon_f^{pt}$$

(52)

Given that the average stress in the CNT phase is given as $\bar{\sigma}_f = C_f \bar{\varepsilon}_f$, using the equivalent inclusion method one can show that the average stress in the CNT phase can be written in terms of the matrix stiffness,

$$\bar{\sigma}_f = C_f \bar{\varepsilon}_f = C_o \left( \bar{\varepsilon}_f - \varepsilon_f^* \right)$$

(53)

where $\varepsilon_f^*$ is the fictitious eigenstrain of the CNT inclusion. For a single ellipsoidal inclusion in an infinite matrix, Eshelby showed that the eigenstrain and perturbed strain of the inclusion can be related via

$$\varepsilon_f^{pt} = S_f \varepsilon_f^*$$

(54)

where $S_f$ is the Eshelby tensor. The components of the Eshelby tensor are provided in Appendix A.
Solving for $\varepsilon^*_f$ in Eq. (53) and then substituting into Eq. (52) using Eq. (54), one can find the dilute strain-concentration factor of the inclusion phase, $A_f^{\text{dil}}$, which relates the average strain in the inclusion to the average strain in the matrix, such that

$$\overline{\varepsilon}_f = A_f^{\text{dil}} \overline{\varepsilon}_o$$

(55)

where

$$A_f^{\text{dil}} = \left[ I + S_f C_o^{-1} \left( C_f - C_o \right) \right]^{-1}$$

(56)

and $I$ is the fourth order identity tensor. We further require that the volume-weighted average phase strains must equal the far-field applied strain, such that

$$v_o \overline{\varepsilon}_o + v_f \overline{\varepsilon}_f = \varepsilon_a$$

(57)

Given Eq. (57), we can now define the strain-concentration factor $A_o$, which accounts for inclusion interactions by relating the average matrix strain in the composite to the uniform applied strain,

$$\overline{\varepsilon}_o = A_o \varepsilon_a$$

(58)

where

$$A_o = \left[ v_o I + v_f A_f^{\text{dil}} \right]^{-1}$$

(59)

The key assumption of the Mori-Tanaka method is that the far-field strain that each inclusion “feels” is the unknown average matrix strain. This can be expressed as

$$\overline{\varepsilon}_f = A_o^{\text{dil}} \overline{\varepsilon}_o$$

(60)

which in conjunction with Eq. (58) gives the strain-concentration factor $A_f$ for the inclusion phase in the non-dilute composite as

$$A_f = A_f^{\text{dil}} A_o$$

(61)
To find the effective stiffness $C$ for a unidirectionally aligned composite, we require that the average stress $\overline{\sigma}$ of the composite be equal to the sum of the weighted average stresses in each phase,

$$\overline{\sigma} = v_o \overline{\sigma}_o + v_f \overline{\sigma}_f = C \varepsilon_a$$  \hfill (62)

Through straightforward substitution and manipulation, the effective stiffness of the unidirectionally aligned composite is found to be

$$C = v_o C_o A_o + v_f C_f A_f$$  \hfill (63)

For the purposes of the next section it is useful to express Eq. (63) in a slightly different form. Recalling Eq. (57) and (62), we can write

$$C = \left( v_o C_o + v_f C_f A_f^{di} \right) \left( v_o I + v_f A_f^{di} \right)^{-1}$$  \hfill (64)

which is a form prevalent in literature. Both Eqs. (63) and (64) thus provide the effective stiffness of a multiphase composite with aligned inclusions. However, in order to account for random orientations of the CNT phase, the analysis must be extended as discussed below.

5.2.2 Mori-Tanaka Method for Randomly Orientated CNTs

When the CNT inclusion phase is randomly orientated in the matrix, determination of the effective composite stiffness can be accomplished by taking the orientational averages of appropriate quantities [189]. In this case the strain consistency condition in Eq. (57) can be written as

$$\left( v_o I + v_f \{ A_f^{di} \} \right) \{ \varepsilon_o \} = \{ \varepsilon_a \}$$  \hfill (65)

where curly brackets $\{}$ represent the orientational average (the average over all possible orientations of the CNT). Due to this averaging process, the average strain in the matrix will be different from that in the unidirectional composite due to the random alignment of inclusions.
Similarly, one can write Eq. (62) for the case of randomly orientated inclusions (noting that because the matrix is isotropic, its stiffness and strain concentration tensors are orientation independent).

\[
\bar{\sigma} = v_o \sigma_o + v_f \left\{ \bar{\sigma}_f \right\} = C \varepsilon_a
\]  \hspace{1cm} (66)

This expression can be simplified using the relationships established in the preceding section.

\[
\bar{\sigma} = \left( v_o C_o + v_f \left\{ C_f A_f^{dil} \right\} \right) \bar{\sigma}_o = C \varepsilon_a
\]  \hspace{1cm} (67)

From Eq. (65) and (67), the effective stiffness of a composite with randomly orientated inclusions can be written as

\[
C = \left( v_o C_o + v_f \left\{ C_f A_f^{dil} \right\} \right) \left( v_o I + v_f \left\{ A_f^{dil} \right\} \right)^{-1}
\]  \hspace{1cm} (68)

which is the direct analog of Eq. (64) except that appropriate averaging is used here to account for the inclusion orientation.

**5.2.3 Orientational Averaging**

As seen in Eq. (68), orientational averages of tensor quantities have to be calculated in order to determine the effective properties of a nanocomposite with randomly orientated CNTs. The orientational average of a tensor is calculated by transforming the tensor from a global to a local coordinate system obtained by rotating the global coordinate system and integrating the transformed tensor over the orientational space.
Figure 5.4 Relationship between the local and global coordinate systems. The local coordinate system is obtained by rotating the global system by angle $\phi_1$ about $X$ and then by angle $\Phi$ about $x'_2$.

Assume the local axes of the CNT are denoted by $x_1'$, $x_2'$, and $x_3'$ (where $x_1'$ is the inclusion axis) and the global axes by $X_1$, $X_2$, and $X_3$ (see Fig. 5.4). The objective is to develop the transformation matrix $a_{ij}$ that maps vector $v_j'$ in the local coordinate system to coordinates $v_i$ in the global coordinate system:

$$v_i = a_{ij}v_j'$$

(69)

In general, it is necessary to specify three Euler angles to describe the orientation of an inclusion, but here, because the inclusion is assumed cylindrical, it is enough to specify only angles $\phi_1$ and $\Phi$ in Fig. 5.4 to completely describe the orientation of the inclusion.

Following the transformations (rotation of axes with respect to the angles specified), the local, $x_i'$, and global, $X_i$, vectors are related by the following:

$$
\begin{bmatrix}
X_1 \\
X_2 \\
X_3
\end{bmatrix} = 
\begin{bmatrix}
p & 0 & q \\
nq & m & np \\
mp & -n & mp
\end{bmatrix}
\begin{bmatrix}
x_1' \\
x_2' \\
x_3'
\end{bmatrix}
$$

(70)

$$m = \cos \phi_1, \ n = \sin \phi_1, \ p = \cos \Phi, \ q = \sin \Phi$$

Eq. (70) can also be written as
\[ X_i = A_{ij}x'_j \]  
(71)

where \( A_{ij} \) represents the transformation matrix for three-dimensional space.

For higher-order tensor transformations, the usual tensor transformation laws are performed. Thus the transformation of a fourth-order stiffness tensor \( C_{ijkl} \) from local to global coordinates can be written as

\[
C_{ijkl}(\phi_1, \Phi) = A_{ir}A_{js}A_{it}A_{ks}C_{rstu}
\]
(72)

where the angular dependence of the \( A_{ij} \) terms is implied and the standard convention that double indices implies summation is used.

Given Eq. (72), the orientational average of a fourth-order tensor in three-dimensional space is

\[
\{C_{ijkl}\} = \frac{1}{2\pi} \int_0^{2\pi} \int_0^\pi C_{ijkl}(\phi_1, \Phi) \sin(\phi_1) d\Phi d\phi_1
\]
(73)

where the transformation matrix for three-dimensional space from Eq. (72) is used in Eq. (73) and the term \( \sin(\phi_1) \) accounts for the surface area of a sphere.

5.2.4 Effective Engineering Constants of Nanocomposite

Once the effective stiffness tensor for the nanocomposite containing either unidirectionally aligned or randomly orientated CNTs is known, the components of the tensor can be used to calculate the engineering constants of the material. We recall that the stiffness matrix for a transversely isotropic material with a 2-3 plane of isotropy can be written as

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{12} & C_{23} & C_{22} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{(C_{22} - C_{23})}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{66} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{bmatrix}
\]
(74)
where the tensoral shear strains $\epsilon_{ij}$ are related to the engineering shear strains $\gamma$ via $\epsilon_{23} = \gamma_{23}/2$, $\epsilon_{13} = \gamma_{13}/2$ and $\epsilon_{12} = \gamma_{12}/2$. The contracted stiffness for a composite with CNTs aligned along the 1-axis will show such a form and the engineering constants can be evaluated using the relationships in Eq. (38). For the case of CNTs randomly orientated in three-dimensional space, the stiffness matrix will be fully isotropic such that the additional relations $C_{22} = C_{11}$, $C_{23} = C_{12}$, and $C_{66} = 1/2(C_{22} - C_{23})$ in Eq. (74) will be satisfied.

For an isotropic material two independent constants are required to describe the material response, for example the Young’s modulus $E$ and the shear modulus $G$. These can be determined from the known stiffness terms via

$$
E = C_{11} - \frac{2C_{12}^2}{C_{22} + C_{23}}
$$

$$
G = \frac{(C_{22} - C_{23})}{2}
$$

5.3 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 [190-192]. 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 finite element concepts coupled with Monte Carlo 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.

5.3.1 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 4.3 of this thesis 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. 3.11 results in the RVE exhibiting a CNT volume fraction of 32% 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. 5.5 which exhibits a Young’s modulus of 460 GPa. This response is used as the constitutive law for the equivalent homogeneous representative fiber. The epoxy matrix, on the other hand, exhibits the constitutive response presented in Fig. 3.8 and follows the same modeling procedure outlined in Section 3.3.3.

Figure 5.5 Constitutive response of RVE for the case of 32% CNT volume fraction.
5.3.2 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 can not accurately describe the geometry for cylindrical and spherical inclusions [193,194]. Hbaieb et al. [194] 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 justification for these values stems from the results of the linear-elastic micromechanical analysis using the Mori-Tanaka method and is presented in Section 7.1.4 of this thesis. 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 [195]. 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. For example, a relatively simplified and unrealistic model utilizing a CNT volume fraction of 0.5%, aspect ratio of 100, and cell length to CNT length ratio of 1:2 already exhibits 200 thousand degrees of freedom deeming the simulation too large to be solved using standard university workstations. 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. The above example 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 listed below and schematically shown in Fig. 5.6.

**Step 1** Construct computational cell using specified dimensions (i.e. cell length = 65 nm).

**Step 2** Disperse representative fiber at a random location with its centroid located within the bounds of the computational cell.

**Step 3** Check if representative fiber extends beyond the boundaries of the cell. If so then truncate the representative fiber and impose periodic boundary conditions.

**Step 4** Check if new truncated segment of representative fiber extends beyond the boundaries of cell. If so then repeat periodic boundary conditions.

**Step 5** Disperse next representative fiber at a random location with its centroid located within the bounds of the computational cell.

**Step 6** Check if representative fiber extends beyond the boundaries of the cell. If so then truncate the representative fiber and impose periodic boundary conditions.

**Step 7** Check if new truncated segment of representative fiber extends beyond the boundaries of cell. If so then repeat periodic boundary conditions.

**Step 8** Check if newest representative fiber segments overlap or contact existing representative segments. If so then delete newest representative fiber segments.

**Step 9** Repeat until required volume fraction of representative fibers has been achieved.
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. Figure 5.7 depicts one such model prior to meshing of the surrounding adhesive and after. The model adopts a CNT aspect ratio of 100 and an RVE volume fraction of 1.56% which corresponds to a CNT concentration of 0.5 vol%.
Figure 5.7 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.
Chapter 6
Experimental Investigations

**Summary:** In this chapter we summarize the different experiments conducted in order to characterize the physical and mechanical properties of nano-reinforced SABs and to further highlight some of the complex phenomena associated with these materials. We describe the dispersion methodology used to introduce the CNTs into the considered adhesive and provide details pertaining to adherent surface preparation, bondline thickness control and adhesive curing conditions. Furthermore, the following tests are described: (i) dogbone tensile testing, (ii) tensile bond testing, (iii) double lap shear and (iv) double cantilever beam fracture toughness testing.

6.1 Fabrication of Nano-Reinforced SABs

6.1.1 Materials Used

The materials used in the experimental program were selected due to their prevalence in aerospace industry. Both aluminum and CFRP are widely used to fabricate structural components in modern aircraft [196]. Furthermore, structural epoxy adhesives represent the largest percentage of adhesives used in this industry [197]. Below we list the materials used in the fabrication of the nano-reinforced SABs and discuss their key mechanical and physical characteristics.

**Carbon Nanotubes**

The CNTs were obtained commercially and synthesized using the electric arc technique. This method creates CNTs through arc-vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar) [198]. A direct current of 50 to 100 A, driven by a potential difference of approximately 20 V, creates a high temperature discharge between the two electrodes. The discharge vaporizes the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode. The carbon arc discharge method is the most common and perhaps easiest way to produce CNTs [199]. However, it is a technique that produces a complex mixture of components, and requires further purification to separate the CNTs from the soot and the residual catalytic metals present.
in the crude product. The purification involves the treatment of the CNTs with nitric acid followed by a cross flow filtration and annealing under a nitrogen atmosphere [200]. The resulting CNTs are extremely high purity (~99.9%) MWCNTs with an outer diameter of 13-18 nm and a length in the range of 1-12 µm. Figure 6.1 (a) - (c) show scanning transmission electron (STEM) micrographs of the as-received MWCNTs at three different magnifications taken with a Quanta 250 field emission gun environmental scanning electron microscope. As can be seen, the CNTs exist as large agglomerates (~5 µm) of MWCNTs that need to be broken up and homogeneously dispersed in the adhesive. Figure 6.2 shows a TEM micrograph of the MWCNTs at a very high resolution allowing one to see the individual fringes formed from the concentric walls of the CNT. Table 6-1 summarizes some of the pertinent properties of the CNTs.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Diameter</td>
<td>13-18 nm</td>
<td>Inner Diameter</td>
<td>308.4</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>407 m²/g</td>
<td>Length</td>
<td>1-12 µm</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>1.0 TPa (in-plane)</td>
<td>Tensile Strength</td>
<td>200 GPa (in-plane)</td>
</tr>
</tbody>
</table>

Table 6-1 Physical and mechanical properties of MWCNTs.
Figure 6.1 STEM micrographs of as-received MWCNTs at different resolutions.
Substrate Materials Selected for Study

Unidirectional carbon fiber sheets and aluminum 6061-T4 were selected as the substrate materials for the different tests programs. Aluminum 6061-T4 is widely used in aircraft and automotive applications [196]. It has excellent joining characteristics, good acceptance of coatings, combines relatively high strength, good workability and high resistance to corrosion. It has a density of 2.7 g/cm$^3$, a tensile strength of 310 MPa, tensile yield strength of 275 MPa, a Young’s modulus of 69 GPa and a Poisson’s ratio of 0.28. The unidirectional CFRP sheets are also widely used in transportation sector and are well accepted for their high strength to weight
ratio. They have a nominal weight per unit area of 290 g/m², while the density of the resin is 1.25 g/cm³. The unidirectional laminate has a fiber volume fraction of 55%, a tensile strength of 1200 MPa, compressive strength of 155 MPa, shear strength of 57 MPa, a tensile modulus of 12 GPa and a Poisson’s ratio of 0.26. The aluminum was used to fabricate tensile pucks and double lap shear substrates while the unidirectional CFRP sheets were used as substrates in the double cantilever beam (DCB) tests.

**Two-Component Epoxy Adhesive**

In this study, we used a two-component epoxy liquid adhesive based on a diglycidyl ether of bisphenol A (DGEBA) and triethylene tetramine (TETA) formulation produced by Hexion Specialty Chemicals. 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 [201]. It is a two-component liquid epoxy typically used in coatings, aerospace and composite applications. It is easily mixed at room temperature and has a low viscosity and excellent environmental resistance. The DGEBA base resin has the designation EPON 825 and is a high purity epoxy resin. As a result, the viscosity of this resin is lower than standard bisphenol A liquid resins without the use of diluents or modifiers. This resin system is used widely in electrical encapsulations and castings, aerospace applications and specialized tooling [202]. The TETA hardening agent has the designation EPIKURE 3046 and is a high purity aliphatic amidoamine with versatile curing capabilities. The optimum properties of the cured epoxy system are obtained at 1:2 parts hardening agent to base resin. Table 6-2 summarizes some of the key physical and mechanical properties of the epoxy system in its cured state.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>46.3 MPa</td>
<td>Tensile Modulus</td>
<td>1.07 GPa</td>
</tr>
<tr>
<td>Tensile Elongation at break</td>
<td>5.5 %</td>
<td>Hardness</td>
<td>83 (shore D)</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>94.8 MPa</td>
<td>Flexural Modulus</td>
<td>2.68 GPa</td>
</tr>
<tr>
<td>Linear Shrinkage</td>
<td>0.0017</td>
<td>Heat Deflection Temperature</td>
<td>73 °C</td>
</tr>
</tbody>
</table>
Dispersing Agent and Surfactants

Carbon nanotubes tend to form ropes or bundles due to strong intermolecular van der Waals interactions. These bundles can aggregate further, forming entangled networks or agglomerates which do not have the optimum mechanical properties of individual CNTs. Thus, great effort has been devoted over the years to prepare stable dispersions of CNTs in different solvents. To date, such CNT dispersions in aqueous media have been reported with the aid of ionic and nonionic surfactants [203-205] and water soluble polymers [206,207]. In aqueous media, surfactants form micelles around the CNTs, preventing reaggregation [203-205,208]. In the case of polymers, the wrapping of nanotube sidewalls is considered to be the mechanism that improves dispersion. Therefore, in order to improve the dispersability of the CNTs in the adhesive and the stability of the resulting dispersion we introduce a compatible surfactant as a form of non-covalent functionalization. The surfactant considered is Polyvinylpyrrolidone (PVP). PVP has already been used to disperse or stabilize CNTs in aqueous environments [204,206,209] but no such records exist for polymeric solutions. The improved dispersability of the CNTs is speculated to be a thermodynamically driven wrapping process of hydrophobic CNTs by the PVP molecules. To demonstrate the stability effect, two CNT solutions were developed using 99% denatured ethanol as the solvent, one with PVP and one without, and time lapse photos were taken over a two month period. Figure 6.3 (a) – (d) show the two solutions at different stages of time with the PVP solution on the right-hand side of the photos. Clearly, the addition of PVP has a significant effect on the stability of the resulting dispersion. After just 10 minutes the CNT solution without PVP has begun to precipitate to the base of the vile and the CNTs have started to agglomerate. After two months’ time the PVP solution is still well dispersed with no sign of agglomeration.
6.1.2 Dispersion Methodology and Specimen Fabrication

The dispersion of the MWCNTs was carried out by first mixing the appropriate quantity of CNTs and in the DGEBA base resin using an overhead mixer at 2000 rpm for 30 mins. The base resin was first heated to 100°C to reduce its viscosity from 5.6 to 0.025 Pa·s. After mixing, the solution was then sonicated using a high intensity ultrasonic processor for 10 mins at 500 W and 40 kHz using a 10 sec ON/OFF cycle to reduce the heat generated by the sonicator. After sonication the solution was cooled to room temperature and placed in a vacuum of 76 cmHg pressure to remove any trapped air. Upon removal from the vacuum the curing agent was added in a 1:2 mix ratio and mixed at 2000 rpm for 30 mins. After mixing, the solution was then applied to the respective substrates and poured into dogbone molds for constitutive response evaluation. The aluminum substrates were shot blasted and cleaned with an isopropanol solution.
prior to bonding. The unidirectional CFRP substrates were also shot blasted and cleaned with a
degreasing agent. A more detailed discussion on the substrate surface preparation methodology
and its effect on the resulting bond strength is presented in Section 7.2.1. The substrates were
then bonded together using specialized polytetrafluoroethylene (PTFE) fixtures coated in a mold
release agent to ensure alignment of the substrates and to allow for easy removal of the test
specimens after curing. The fixtures are depicted in Fig. 6.4. Glass beads of 0.4 mm diameter
were added for bond line thickness control. The samples were cured at 25°C for 24 hours
followed by 2 hours at 100°C. Samples with MWCNT weight concentrations from 0.0 to 3.0
wt% in 0.5 wt% increments were developed.

![Test specimen layup fixtures.](image)

### 6.2 Mechanical Characterization of Nano-Reinforced SABs

#### 6.2.1 Dogbone Tensile Testing

The dogbone tensile test was used to evaluate the Young’s modulus and maximum tensile
strength of the nano-reinforced adhesive. The test was carried out as per the ASTM D638-10 test
standard using the specimen dimensions shown in Fig. 6.5 (a). The dogbone test specimens
where fabricated by pouring the adhesive into specialized molds made from PTFE and coated in
a mold release agent as shown in Fig. 6.5 (b). The dogbone specimens were then permitted to
cure and were removed from the mold using pushout pins located in the back of the mold. The
specimens were then sanded using a belt sander to achieve a uniform thickness across the entire
length. The test was carried out using an electro-hydraulic servo-controlled testing machine at a
loading rate of 5 mm/min and equipped with an extensometer for accurate displacement
measurement.
6.2.2 Tensile Button Testing

Figure 6.6 (a) shows a schematic diagram of the test setup used during the tensile button testing for the evaluation of the tensile bond strength of nano-reinforced SABs. The load was applied perpendicular to the bonding plane and the test procedure was carried out as per the ASTM D897-1 standard requirement. The test used circular pucks machined from aluminum 6061-T4 with a circular plane bonding area of 28.5 mm in diameter as depicted in Fig. 6.6 (b). The test was carried out using an electro-hydraulic servo-controlled testing machine equipped with specialized crosshead adaptors shown in Fig. 6.6 (c) at a speed of 127 mm/min. Load co-axiality was ensured using the crosshead adaptors and strain gauged samples. The bond line thickness was controlled at 0.4 mm using glass beads.

6.2.3 Double Lap Shear Testing

The double lap shear (DLS) test setup shown in Fig. 6.7 (a) was used to evaluate the shear strength of the nano-reinforced SABs. The load was applied parallel to the bonding plane and the test procedure was carried out as per the ASTM D3528-96 test standard. The test specimens shown in Fig. 6.7 (b) were fabricated from aluminum 6061-T4 and exhibited an overlap bonding area 10 mm in length and 25.4 mm in width. The same electro-hydraulic testing machine and
loading rates used in the tensile adhesive bond test were used in the evaluation of the shear bond strength. The influence of the stiffness of the loading bars and machine crosshead was considered during the tensile and shear testing of the nano-reinforced SABs. The compliance of the machine was subtracted from the load-displacement results reported in this work. At a load of 2.5 kN the maximum observed displacement was 0.035 mm and 0.053 mm at a load of 5 kN.

Figure 6.7 (a) Schematic illustration of DLS test, and (b) final DLS test specimens.

6.2.4 Double Cantilever Beam Testing

Susceptibility to delamination is one of the major weaknesses of many advanced laminated composite structures [210]. Knowledge of a laminated composite material’s resistance to interlaminar fracture is useful for product development and material selection. Furthermore, a measurement of the Mode I interlaminar fracture toughness $G_{IC}$, independent of specimen geometry or method of load introduction, is useful for establishing design allowables used in damage tolerance analyses of composite structures made from these materials. The double cantilever beam (DCB) test was used to evaluate the Mode I interlaminar strain energy release rate, $G$, and was tested according to the ASTM D5528-1 test standard. A schematic of the test is shown in Fig. 6.8. Each specimen consists of two rectangular, uniform thickness, unidirectional laminated CFRP sheets bonded together by the nano-reinforced adhesive. The specimens contain a 13µm thick non-adhesive PTFE insert on the midplane plane which serves as a delamination initiator. In the DCB test, as the delamination grows from the insert, a resistance-type fracture behavior typically develops where the calculated $G_{IC}$ first increases monotonically, and then stabilizes with further delamination growth. In this test method, a resistance curve ($R$ curve) depicting $G_{IC}$ as a function of delamination length is generated to characterize the initiation and propagation of a delamination in a unidirectional specimen. Opening forces are applied to the DCB by means of upper and lower loading blocks bonded to one end of the specimen. The front
end of the specimen is opened by controlling the loading block displacements through the crosshead movement while the load and opening displacement are recorded. The test was carried out using an Instron 5800 MicroTester with a crosshead speed of 0.5 mm/min. A high resolution optical microscope with a data acquisition link to a computer interface is used to instantaneously monitor the position of the advancing delamination front at a resolution of 100 µm. The microscope is mounted on travelling stages to provide the movement in the x-z plane. The DCB test rig is shown in Fig. 6.9 along with the individual components clearly labeled.

Figure 6.8 Schematic illustration of DCB test specimen.

Figure 6.9 DCB Testing rig and traveling optical stage.
In the DCB test we measure the influence of the dispersion of CNTs on the Mode I strain energy release rate of adhesively bonded composite joints. The Mode I strain energy release rate is defined as the loss of energy, \( dU \), in the test specimen per unit of specimen width for an infinitesimal increase in delamination length, \( da \), for a delamination growing under a constant displacement. In mathematical form,

\[
G = \frac{1}{b} \frac{dU}{da}
\]  

(76)

The corrected beam theory method was used to calculate the energy release rate values, such that:

\[
G = \frac{3P\delta}{2b(a + \Delta)} \frac{F}{N}
\]

(77)

where \( P \) is the applied load, \( \delta \) is the load point displacement, \( b \) is the specimen width, and \( \Delta \) is a correction factor to account for any possible rotation at the delamination front. \( \Delta \) was determined experimentally by generating a least squares plot of the cubic root of compliance. \( F \) and \( N \) are correction factors for nonlinear large deformation and the stiffening effect of the loading hinges, respectively:

\[
F = 1 - \frac{3}{10} \left( \frac{\delta}{a} \right)^2 - \frac{3}{2} \frac{\delta t}{a^2}
\]  

(78)

\[
N = 1 - \left( \frac{L'}{a} \right)^3 - \frac{9}{8} \left[ 1 - \left( \frac{L'}{a} \right)^2 \right] \left( \frac{\delta t}{a^2} \right) - \frac{9}{35} \left( \frac{\delta}{a} \right)^2
\]

(79)

where \( L' \) and \( t \) are dimensions relating to the loading blocks.
Chapter 7
Analysis of Results and Discussions

Summary: This chapter is divided into three main sections. The first is concerned with the numerical predictions using the newly proposed multiscale methodology. Specifically, we present the constitutive response of CNT structures, their interfacial characteristics, and the homogenized properties of the bulk composite using micromechanics and homogenization techniques. The second is concerned with the experimental findings and the influence of the proposed dispersion methodology on the tensile, shear and fracture toughness properties of the nano-reinforced SAB. Finally, comparisons between the numerical predictions and experimental findings are presented.

7.1 Numerical Predictions
7.1.1 Constitutive Response and Fracture Behavior of CNT

In this thesis, the nonlinear response of individual CNTs under mechanical loading is investigated. Two CNT arrangements were studied: (16,0) zigzag nanotube and (9,9) armchair nanotube, both having diameters of approximately 1.2 nm. Tensile and torsional loading conditions were investigated to obtain tensile and shear properties. In both cases, one end of the nanotube was completely restrained, while the other end was assigned a prescribed displacement. In computation, a pristine nanotube does not present a favorable location for fracture to nucleate due to the intrinsic symmetry of the defect-free nanotube structure. Instead, fracture will often nucleate simultaneously at multiple locations along the length of the tube. However, when the nanotube end is restrained with a rigid boundary constraint, stress concentrations near the constrained end are inevitable. Such an effect is likely to cause the bond lengths and bond angles near the tube ends to be different from the remaining part of the CNT. This will cause the nanotube to fail at the restrained end which is unrepresentative of the realistic failure process. In order for the nanotubes to fail elsewhere along their length, a defect must be introduced in the graphene lattice. In this study, a 5% weakening of a bond located halfway along the CNT length is introduced to initiate fracture in the desired location. A CNT length of 7 nm was determined to be sufficient in avoiding the effects of the constrained boundary conditions.
In typical atomic level simulations, the force acting in a structure is a more meaningful measure than the stress. However, in order to present the results in a universally recognized form and for the sake of comparison, it was decided to derive the uniaxial stress and plot it against the applied strain, $\varepsilon$, computed by $\varepsilon = (L - L_o)/L_o$, where $L$ is the deformed length and $L_o$ is the initial length of the nanotube. To do so, a corresponding area must be defined. Here, the cross-sectional area is defined as $A_o = \pi D t$, where $D$ is the diameter of the nanotube and $t$ is the thickness taken to be equal to 0.34 nm. Therefore, we can define the uniaxial stress acting in the nanotube as

$$\sigma = \frac{F_\sigma}{A_o} = \frac{F_\sigma}{\pi Dt}$$ (80)

where the total axial force, $F_\sigma$, is obtained by summing the interatomic forces acting on the atoms at the restrained end of the CNT.

The predicted tensile stress-strain curves for both armchair and zigzag CNT arrangements are presented in Fig. 7.1, while the corresponding mechanical properties are provided in Table 7-1. From the stress-strain curves, we can see that the zigzag nanotube can withstand a strain of 17.5%, while the armchair nanotube can withstand a strain of up to 20.7%. The respective Young’s modulus for the armchair and zigzag nanotubes are 944.8 GPa and 920.2 GPa. The tensile strength is predicted to be approximately 114 GPa and 93 GPa for armchair and zigzag configurations, respectively. In comparison, the experimental tensile measurements of Demczyk et al. [211], using a piezoelectric manipulator within a TEM, observed a Young’s modulus of approximately 900 GPa and a corresponding tensile strength of 150 GPa for a generic SWCNT. The overall trend of the stress-strain curves also agree well with other numerical works in the literature [161,162,212,213], and also show that the armchair configuration exhibits higher strength and stiffness when compared to the zigzag configuration. Figure 7.1 leads us to deduce that given the appropriate bonding, dispersion, and alignment, the armchair nanotube will act as a better reinforcing agent in composite materials, when compared to the zigzag configuration.
Table 7-1 Tensile properties of armchair and zigzag carbon nanotubes.

<table>
<thead>
<tr>
<th>Property</th>
<th>Zigzag (16,0)</th>
<th>Armchair (9,9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>920.2</td>
<td>944.8</td>
</tr>
<tr>
<td>Maximum Tensile Stress (GPa)</td>
<td>93.4</td>
<td>114.4</td>
</tr>
<tr>
<td>Maximum Tensile Strain (%)</td>
<td>17.5</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Figure 7.1 Constitutive response of zigzag and armchair CNTs under tensile load.

It should be noted that the Modified Morse potential is not appropriate for describing the behavior of CNTs after bonds are broken since it does not consider the formation of new bonds and the possibility that rehybridization and structural transformations may occur. However, it has been shown that the fracture strength of CNTs depends primarily on the inflection point of the potential [161]. Therefore, since the inflection strain occurs well before the strain required to break bonds and form new ones, we are provided with some confidence that the Modified Morse potential can give a correct picture of the tensile properties of CNTs up to failure. Also, from both experimental [38] and theoretical studies it has been determined that the stress suddenly drops to zero once the maximum tensile strength has been reached. Therefore, the reported maximum stresses and strains corresponding to the inflection point on the stress-strain curves are taken as the tensile capacity of the nanotube.

Of interest to the present study are the deformation mechanisms of CNTs under both tensile and torsion loading conditions. Figure 7.2 (a) and (b) show the tensile fracture process for both armchair and zigzag nanotubes, respectively. For both cases the nanotubes simply elongate with
little reduction in their cross-sectional area until they fracture. Fracture initiates at the weakened bond. For the case of the armchair nanotube, fracture occurs gradually. At 17.4% strain, the first bonds are broken which leads to the successive elongation and failure of neighboring bonds. At a critical strain of 20.7% all the bonds along the circumference of the nanotube have broken. In this case, the bonds fail in an irregular pattern and give rise to a large hole on the surface of the CNT. For the case of the zigzag nanotube fracture occurs almost instantaneously. At a strain of 16.6% the weakened bond has reached its critical strain and breaks, which causes the adjacent bonds along the circumference of the nanotube to take up the load. At a strain of 17.5% nearly all the adjacent bonds have broken and the zigzag nanotube has fractured. From this we can conclude that the zigzag nanotube exhibits brittle behavior at fracture. Also, the fracture process resembles the propagation of an ideal crack through the nanotube in a direction orthogonal to the nanotube longitudinal axis.

We can attribute the differences in strength, strain at fracture, and the fracture processes to the orientation of the bonds in the nanotube structures. For the case of the zigzag nanotube a large percentage of the bonds are orientated parallel to the axial loading direction. Thus, these bonds tend to carry most of the load and subsequently undergo larger elongations. In the case of the armchair nanotube, most of the bonds are orientated at a 30 degree angle to the loading direction. This causes the bonds to fail in an irregular pattern at larger strains. Figure 7.3 plots the elongation of the weakened bonds in both structures against the axial strain of the nanotube. The results are only extended to a critical bond elongation of 0.027 nm which corresponds to the 19% inflection strain of the Modified Morse potential. The figure clearly confirms that the bond in the
zigzag nanotube reaches its critical elongation at lower axial nanotube strain values when compared to the armchair nanotube. The tensile fracture process for both armchair and zigzag configurations are in agreement with those of Belytschko et al. [161], Lu and Bhattacharya [214], and Meo and Rossi [213].

![Graph showing elongations of weakened bonds plotted against the axial strain of the CNT.](image)

Figure 7.3 Elongations of weakened bonds plotted against the axial strain of the CNT.

The CNT was simulated with a diminishing rotational spring element stiffness to demonstrate the effect of omitting the angle bending component of the Modified Morse potential. The corresponding stress-strain curve is provided in Fig. 7.4. As can be seen, the CNT provided no response to the initial loading. This can be attributed to the fact that the bending of adjacent bonds is responsible for the initial deformation of the CNT. The initial elastic stretching of a nanotube occurs due to the elongation of the hexagons in the nanotube wall by way of adjacent bonds bending relative to each other and not by the stretching of the individual bonds themselves. Without the angle bending component of The Modified Morse potential the CNT tends to collapse on itself or slacks, as depicted in Fig. 7.5 for the case of the zigzag nanotube, until enough loading has been applied to stiffen the structure. However, apart from this initial stiffening effect, the angle-bending component contributes insignificantly to the overall fracture behavior of the CNT. Therefore, it can be concluded that the bond angle bending component of the Modified Morse potential is essential in establishing an equilibrium configuration of the nanotube but plays no role in the fracture process. The same behavior has been observed by Belytschko et al. [161] in their atomistic simulations of nanotube fracture.
Figure 7.4 Effect of omitting the bond angle bending component of Modified Morse potential on the constitutive response of a CNT under tensile load.

As in the case of the tensile loading scenario it is also useful to define the shear stress due to torsion so that the results may be presented in a recognized form. Here, the shear stress is defined in a similar manner to the above uniaxial stress ($\tau = F_{\tau} / A_o$) where the cross sectional area also remains the same, however, the total shear force, $F_{\tau}$, is now computed by summing the reaction forces acting in the tangential direction of all the atoms at the restrained end of the nanotube. The shear strain is defined as $\gamma = r\Delta \theta / L_o$, where $r$ is the radius of the nanotube, $\Delta \theta$ is the rotation of
the nanotube around the z-axis, and $L_o$ is the initial length of the nanotube. The shear loads were induced by applying a prescribed tangential displacement at the free end of the nanotube while restraining the axial and radial displacements.

The shear stress-strain curves for both types of nanotubes are shown in Fig. 7.6 along with the corresponding properties of relevance in Table 7-2. The shear modulus for zigzag and armchair nanotubes was predicted to be 344.2 GPa and 343.4 GPa, respectively. These values do agree with several quoted values in literature [59,215,216]. For example, Giannopoulos et al. [59] developed a nanotube model using a spring-based finite element approach. They used simple harmonic potentials to derive the stiffness of the elements in their model. However, instead of using beam elements, Giannopoulos et al. used truss rods to model individual C-C bonds as well as the bond-angle bending component of the potential. The average value over a sample size of ten different chiralities was given as 324.5 GPa. The shear stress-strain curves also show good overall agreement with those presented by Xiao et al. [217]. In their paper, the predicted shear strength for both armchair and zigzag nanotubes was 108 GPa with corresponding failure strains in the range of 27% to 33%. In comparison, the present study has predicted shear strengths of 105 GPa and 111 GPa for armchair and zigzag nanotubes, respectively, with corresponding failure strains of approximately 38% and 37%. From Fig. 7.6 it can also be concluded that the shear stress-strain relationships are approximately linear up to their critical values which indicate that the shear modulus is insensitive to the strain.

![Figure 7.6 Constitutive response of armchair and zigzag CNTs under torsional load.](image-url)
Table 7-2 Shear properties of armchair and zigzag carbon nanotubes.

<table>
<thead>
<tr>
<th>Property</th>
<th>Zigzag (16,0)</th>
<th>Armchair (9,9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear Modulus (GPa)</td>
<td>344.2</td>
<td>343.4</td>
</tr>
<tr>
<td>Maximum Shear Stress (GPa)</td>
<td>111.1</td>
<td>105.5</td>
</tr>
<tr>
<td>Maximum Shear Strain (%)</td>
<td>37.0</td>
<td>38.0</td>
</tr>
</tbody>
</table>

Figure 7.7 (a) and (b) show the torsional deformation process for both armchair and zigzag nanotubes, respectively. In torsion, the nanotubes first twist with little or no change in their cylindrical geometry until an approximate shear strain of 15% and 25% for armchair and zigzag nanotubes, respectively. At this shear strain, the nanotubes begin to show localized collapse or the onset of torsional buckling. It is also at these corresponding strains that the shear stress-strain curves begin to deviate from their initial linear behavior. These shear strains correspond to an angle of twist equal to 1.33 rad and 2.09 rad for armchair and zigzag nanotubes, respectively. Therefore, it is probable that nanotubes with a zigzag structure possess higher resistance to torsional buckling than the armchair nanotubes. At respective critical shear strains of approximately 38% and 37%, the armchair and zigzag nanotubes have collapsed entirely in the localized zone and take the form of straight axis spirals. The observed torsional deformation processes are consistent with those observed both theoretically by means of molecular dynamics simulations by Yakobson et al. [57], Aghaei and Dayal [218] and experimentally by Yu et al. [219]. Aghaei and Dayal also observed a primarily linear response to an applied torsional load to the onset of buckling.
7.1.2 ABC Model Validation Using Molecular Dynamics

In order to validate the ABC model and confirm the accuracy of the presented results, MD simulations were conducted employing two different many-body potentials using the LAMMPS MD software. The two selected interatomic potentials are the Tersoff potential and the AIREBO potential. Both potentials are of the many-body form and include additional interaction effects in their formulations which improve their accuracy over the Modified Morse pair potential.

One distinct CNT structure was investigated, a 12 nm (9,9) armchair nanotube with an axial deformation rate of 1.0 Angstroms/0.0005 picoseconds to suppress any boundary effects. The CNT was first equilibrated using NPT ensemble which ensures constant pressure and temperature for a total of 20000 timesteps. Loading of the CNT was then achieved by prescribing a displacement to the upper atoms of the CNT structure over 1 million timesteps with an equilibrating run after each step. In all cases the timestep size was 0.0005 picoseconds. The
results are compared to the ABC predictions presented above which employed the Modified Morse pair-potential. Figure 7.8 compares the predicted stress-strain profiles for all three cases. Clearly, both models compare extremely well with the predictions of the ABC model. However, the AIREBO model seems to underestimate the constitutive response when compared to the other cases. Both potentials also seem to predict higher tensile strains when compared to the ABC model. Table 7-3 summarizes the pertinent properties of interest for all three cases. It should be noted that the tensile stress-strain curves for the MD models depicted in Fig. 7.8 are polynomial curve fittings to the raw data which normally include substantial fluctuations.

![Figure 7.8 Comparison of ABC and MD constitutive response predictions for the tensile loading of a (9,9) armchair nanotube.](image)

<table>
<thead>
<tr>
<th>Model</th>
<th>Young’s Modulus (GPa)</th>
<th>Maximum Tensile Stress (GPa)</th>
<th>Maximum Tensile Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABC</td>
<td>944.8</td>
<td>114.4</td>
<td>20.7</td>
</tr>
<tr>
<td>MD Tersoff</td>
<td>1103.7</td>
<td>119.2</td>
<td>27.7</td>
</tr>
<tr>
<td>MD AIREBO</td>
<td>883.0</td>
<td>107.8</td>
<td>24.4</td>
</tr>
</tbody>
</table>

Table 7-3 Comparison of pertinent mechanical properties for the different cases considered.

In order to compare the fracture behavior of the models, one bond located along half the CNTs length was weakened by 5% as was done for the case of the ABC model. Figure 7.9 depicts the tensile fracture process for both MD cases. When compared with fracture process of the ABC model depicted in Fig. 7.2, it becomes evident that the ABC model better replicates the MD case
employing the Tersoff potential, which also predicts a ‘tearing’ effect along the circumference of the nanotube. The AIREBO model, on the other hand, predicts a ‘un-coiling’ type fracture process and also indicates failure of the bonds near the boundary which may be indicative of boundary artifacts.

Figure 7.9 Nanotube deformation process under tensile loading using (a) the Tersoff potential and (b) the AIREBO potential.
Evidently, the proposed ABC modeling scheme compares well with traditional MD approaches employing complex many-body potentials. These potentials account for additional quantum interaction effects when compared to their pair-wise counterparts. This seems to justify the proposed modeling technique and the choice of the Modified Morse potential in the ABC modeling of CNT structures. Furthermore, we can conclude that long range interactions are insignificant for these particular nanoscale structures.

### 7.1.3 Interfacial Characteristics

The mechanical properties of a composite material are governed by the characteristics of the reinforcing filler-polymer matrix interface. The interface is largely responsible for stress transfer from the surrounding matrix to the reinforcement. As such, the extremely high aspect ratios of CNTs lend themselves to greatly improve the transferability of load at the interface, when compared with conventional microfibers. Furthermore, crack-bridging and CNT pullout play an important role in toughening of CNT based composites and their dominance is also largely dictated by the conditions of the interface and the intrinsic strength of the CNT. Crack-bridging is favored when the strength of the interface exceeds that of the reinforcing CNT whereas the pull-out toughening mechanism favors a weak interface. Both mechanisms show great potential to improve the fracture toughness of the said composite. For example, the maximum tensile strength of a SWCNT can reach upwards of 120 GPa as predicted by our current simulation technique [195] and in some cases the ISS can reach upwards of 500 MPa as reported by Wagner and co-workers based on fragmentation tests in urethane-CNT composites [102]. Therefore, it becomes desirable to investigate the properties of the interface in order to provide greater insight into these key toughening mechanisms.

The key parameters to be investigated are the CNT embedded length and CNT diameter. Both have been analytically shown to have a significant impact on the resulting composite toughness as evidenced by the following equation from the classic article by Kelly [220] which describes the average pullout energy per fiber:

\[
G_f = \frac{1}{12} \pi r t L^2
\]
where $r$ is the radius of the reinforcing fiber, $\tau_i$ is the ISS, and $L$ is the embedded length. In addition, we highlight the importance of CNT capping, the polymer morphology around the embedded end of the CNT and interfacial strengthening through chemical bond formation.

**Pull-Out Experiment**

To investigate the interfacial properties of a CNT-polymer composite system a pull-out test of the nanotube is simulated whereby the CNT is withdrawn from the surrounding matrix and the pull-out forces are recorded. The present study uses the modeling approach presented in Chapter 4 of this thesis and we consider both a generic thermoset polymer and a specific two-component epoxy system. The generic polymer system will allow for us to identify the effect of polymer morphology and atomic density in the region surrounding a CNT on the ISS while the specific two-component system allows for more detailed investigation into the parameters that affect the interfacial properties. 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 can then be calculated 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 nanotube, respectively. Figure 7.10 depicts a simulated pull-out profile (pull-out force vs. pull-out distance) for the generic polymer system. After an initial loading segment, a sliding or steady state regime ensues as the nanotube is gradually pulled through the surrounding matrix. The pull-out force then decreases as the end of the CNT approaches the upper surface of the polymer matrix. One can observe that the pull-out force exhibits relatively little variation in the sliding regime. However, this is not a common characteristic of all predicted pull-out profiles. Rather the smoothness of the sliding regime is due to a high polymer nodal density and the ordered and uniformly distributed polymer nodal representation. In this generic study, the interface region is saturated with a high number of vdW interactions which prevents any sharp oscillations in the pull-out force as the CNT is withdrawn from the matrix. It is worth noting that the work also includes the effect of a random distribution of the polymer atoms, as explained later on, and this will result in sharp peaks and valleys in the pull-out profile which correspond regions of high and low vdW interactions during the respective pull-out process. The general pull-out profile depicted in Fig. 7.10 shows striking resemblance with those obtained by Xia and Curtin [221] in their MD studies of the sliding behavior of MWCNTs. This MWCNT “sword-and-sheath” deformation can also be viewed as a composite system wherein the outer walls represent a matrix material surrounding a broken
nanotube. In comparison, pull-out profiles obtained experimentally via the direct tensile loading of the CNT using an AFM setup do show discrepancies. For example, the results of Barber et al. [103] show an initial rise in the pull-out force until a critical force is reached at which point the interface is thought to have failed and a large drop in the force is subsequently observed with no evidence of a sliding regime (Fig. 7.11 (a)). A similar profile is observed in the experimental results of Cooper et al. [100] using a SEM setup (Fig. 7.11 (b)). These discrepancies can be explained as follows. The present study treats the CNT as a continuous fibre that extends the same distance as the surrounding matrix in the RVE. As such, it does not take into account the end effects that may result from the capping of the CNT and the added vdW interactions that would occur if the base of the CNT were also embedded in the polymer. These end effects would significantly increase the peak pull-out force during the initial stages of loading as will be shown in Section 7.1.3.6.

Figure 7.10 Typical pull-out profile for a CNT embedded in a generic polymer.
The discrepancies between experimentally observed and simulated profiles can also be explained by the time scale over which the pull-out process occurs. Once the interface fails, the subsequent sliding of the nanotube occurs quite rapidly. It is believed that experimental techniques are hindered by the temporal resolution of the equipment used and are incapable of attaining sufficient measurements to capture this sliding regime. Furthermore, the experimental works are unable to ensure a perfect non-bonded system as the one investigated in the present work. As a result, the CNT polymer system considered in these works may in fact have a degree of functionalization present which could explain the sharp peak evident in their pull-out profiles.

**Effect of van der Waals Interactions**

In this study, the polymer matrix is represented by a series of nodes forming concentric cylinders around the reinforcing nanotube space-frame structure. We feel that this description forms an adequate basis on which the interfacial properties of a generic polymer CNT system can be investigated. The density of nodes in the polymer description will determine the number of vdW interactions between the CNT and the surrounding polymer, and consequently, the resulting ISS. To study the sensitivity of this parameter on the ISS, the number of nodes in the polymer representation is varied. Three studies are conducted to investigate the effect of polymer atomic density, or equivalently, the number of vdW interactions. In each study, a CNT of 1.776 nm in length and an interfacial thickness of 0.34 nm is used. The first study considers only the immediate surrounding layer of the polymer and varies its number of nodes. In the second study, the number of nodes in the polymer layers remain constant but the number of layers surrounding the CNT is increased using an interlayer spacing of 0.1275 nm. This interlayer spacing was
selected to ensure a uniform distribution of the nodes throughout the polymer volume. The third study utilizes a computational cell of constant volume that extends 1.0 nm into the surrounding polymer. This study considers variations in the proximity of the layers and the number of vdW interactions are varied by increasing the number of layers in the defined volume. In all three studies, the chemical composition of the polymer is ignored, implying that only carbon-carbon vdW interactions are considered. A schematic of the three studies considered is provided in Fig. 7.12.

![Figure 7.12 Schematic diagram of polymer representations used to study the effect of vdW interaction density using (a) only the inside polymer surface (Study 1), (b) multiple polymer layers with a constant interlayer spacing (Study 2), and (c) a constant volume with varied interlayer spacings (Study 3).](image)

Four interfacial configurations are considered in Study 1 with vdW interaction densities ($\delta$) corresponding to 5000, 10000, 19000 and 37000 vdW interactions per square nanometer CNT (int/nm$^2$), respectively. The vdW interaction density represents the total number of vdW interactions occurring during the pull-out process divided by the surface area of the nanotube. Figure 7.13 shows the predicted linear dependency of the ISS on the vdW interaction density for the case where only the immediate surrounding layer of the polymer was considered. Figure 7.14 shows the effect of vdW interaction density on the ISS for studies 2 & 3. In both studies the ISS increases with increasing number of layers and interaction density. However, in study 2 the number of layers considered does not seem to have a significant effect beyond the fourth layer. This study used a constant interlayer spacing and successively added more layers to the surrounding polymer. The ISS begins to plateau because as more layers are added, the atoms are situated at a further distance from the CNT. The corresponding vdW interactions become weaker due to the large atomic separation distance. For example, the fifth layer is situated at a radial distance of 0.85 nm from the wall of the CNT. This distance also corresponds to the traditional
LJ cut-off distance used in MD simulations where the potential is truncated to ignore interactions that extend beyond this distance. Study 3, however, does show a continually increasing ISS with increasing number of layers and interaction density. This study used a computational cell of constant volume. As more layers are added to the cell their interlayer spacing decreases. This also shifts some of the atoms to within a closer distance of the CNT resulting in stronger vdW interactions thus increasing the ISS. The trend observed in study 3 seems to exhibit a similar linear dependence as in study 1.

Figure 7.13 The effect of the vdW interaction density on the interfacial shear strength when only the inside surface of polymer is considered.

Figure 7.14 The effect of the vdW interaction density on the interfacial shear strength when multiple polymer layers are considered.
The above three studies can be used to help identify the effect of polymer morphology and atomic density in the region surrounding a CNT on the ISS of a generic polymer CNT system. However, one cannot extrapolate a value from these results for a specific polymer system. For the sake of completeness we present a final study for which a reasonable estimate of the ISS of a specific two-component epoxy polymer CNT system is predicted. This system is used as the computational model for the remaining analyses of this section. A simple epoxy resin based on DGEBA and a common curing agent, TETA, is selected.

Using the model shown in Fig. 4.5 to model the surrounding epoxy, the ISS for the two-component epoxy system of 6.60 nm in length is predicted to be 21.98 MPa and the corresponding pull-out profile is depicted in Fig. 7.15. In comparison, Zheng et al. [112] predicted a non-bonded ISS of approximately 33 MPa for a CNT of 5.9 nm in length embedded in a polyethylene matrix via MD. The results are comparable and any discrepancies can be attributed to differences in the CNT diameter and the different polymer systems investigated.

Effect of CNT Embedded Length

Figure 7.16 shows simulated pull-out profiles for nanotubes of three different lengths; 3.3 nm, 6.6 nm, and 12.8 nm with an interfacial thickness of 0.34 nm. At first glance one may conclude that the maximum pull-out force increases with embedded CNT length, particularly when comparing the 6.6 and 12.8 nm profiles. However, the additional sharp peaks evident in the 12.8 nm profile are due to the random distribution of nodes in the polymer representation. If a
uniform distribution of nodes were adopted the profiles would exhibit a smoother and more consistent plateau regime. For example, Fig. 7.17 depicts the pull-out profiles for three different lengths when using the polymer representation of Study 1. As can be seen the pull-out profiles show very little variability and the maximum pull-out force is identical for all three lengths. Therefore, it can be inferred that the maximum pull-out force remains relatively unchanged for CNTs of different lengths. This can be explained by reference to stress distributions in traditional fiber pull-out tests. It is well known that for the case of a continuous fiber composite with a load applied in the fiber direction there exists both normal and interfacial shear stresses. However, the distribution of these stresses differs along the embedded length of the fiber. The normal stresses vary linearly from a maximum at the loaded end of the fiber to zero at the embedded fiber end. The interfacial shear stresses, on the other hand, rise exponentially and peak at either the loaded or embedded ends depending on the material properties of the constituent materials [222]. A similar interfacial shear stress distribution is observed in the present nanotube pull-out simulation. At the nanoscale, only vdW interactions participating with CNT atoms near the loaded end of the nanotube contribute to counteract the applied pull-out force. A two-dimensional schematic depiction of the vdW interactions at the interface is provided in Fig. 7.18. The vdW interactions acting on CNT atoms along the length of the nanotube have no cumulative effect on the pull-out force and ISS. Instead, the cumulative resultant vdW force is normal to the longitudinal axis of the nanotube and hence to the direction of nanotube loading. In comparison, the CNT atoms near the end of the nanotube have a component of the cumulative force opposing the pull-out force which contributes to the ISS. Therefore, increasing the CNT embedded length has no effect on the maximum pull-out force of non-bonded nanotubes; rather it only serves to extend the sliding regime of the pull-out profile, as depicted in Fig. 7.17. Given that the maximum pull-out force is not affected by the CNT length, it is expected that longer CNTs will transfer the stress developed over the interface more effectively. Similar conclusions regarding the effect of embedded length on the pull-out force and the general trends of the pull-out profiles were drawn by Li et al. [223] in their MD pull-out studies of capped and uncapped CNTs in polymer and alumina nanocomposites, the analytical study of Ahmed and Keng [224] on the stress distributions in perfectly bonded CNT polymer composites, and the MD work of Pavia and Curtin [225] which investigates the pull-out forces of CNT-diamond composites.
Figure 7.16 Pull-out profiles for CNTs with different embedded lengths in the two-component epoxy formulation.

Figure 7.17 Pull-out profiles for CNTs with different embedded lengths in the generalized polymer formulation.

Figure 7.18 Two dimensional schematic depiction of the cumulative resultant vdW forces along the length of a CNT during the pull-out process.
Effect of Interfacial Thickness

A number of approaches have been considered to account for the interfacial properties of CNT polymer composites. These depend on the type of bonding, type of polymer matrix, and load transfer mechanisms considered. Hence, the interfacial thickness has not yet been unambiguously defined. Several different values have been used in both atomistic and continuum simulations. Hu et al. [226] simulated the helical wrapping of one polystyrene chain around a CNT considering only van der Waals interactions via molecular dynamics. The equilibrium distance between the hydrogen atoms in the polymer and carbon atoms in the nanotube ranged from 0.2851 to 0.5445 nm. However, only one polymer chain was considered, while in practical cases there may be other chains which also wrap around the nanotube. In comparison, Li and Chou [144] studied the compressive behavior of CNT/polymer composites and assumed that the inside surface of the polymer matrix was located at the same position as the outside surface of the nanotube, giving an interfacial thickness equal to 0.17 nm or half the thickness of the nanotube itself. Montazeri and Naghdabadi [178] used an interfacial thickness of 0.3816 nm in their molecular structural mechanics model of SWCNT-polymer composites. This value corresponds to the equilibrium distance of the Lennard-Jones potential. Given the above variance, it is worthwhile to investigate the effect of different interfacial thicknesses on the ISS of the CNT polymer composite system.

Figure 7.19 shows the predicted ISS for the two-component epoxy system over an interfacial thickness range of 0.30 to 0.46 nm for a CNT of 3.30 nm in length. An immediate observation is that the ISS increases with decreasing interfacial thickness. The present analysis adopts a constant computational volume that extends a radial distance of 1.0 nm from the wall of the CNT. As the interfacial thickness is decreased, a larger number of polymer atoms are included in the computational cell which increases the number of vdW interactions occurring over the interface and the subsequent ISS.
Effect of CNT Diameter

The use of CNTs as reinforcing agents in epoxies allows for nanotubes with various diameter ranges to be selected. The diameter of a CNT can have an effect on its macroscopic reinforcement properties, which needs to be understood. Here, we examine five nanotubes of length 4.2 nm embedded in the two-component DGEBA/TETA polymer representation. Armchair configurations are considered, with the smallest being a (5,5) nanotube, and the largest an (18,18) nanotube. In order to minimize the effect of polymer distribution on the pull-out curves, an identical polymer configuration is used for all simulations, and polymer atoms outside the 0.34 nm – 1.34 nm interfacial range are deleted after modeling the nanotube. Figure 7.20 shows the pull-out profiles predicted for CNTs of different diameters while Fig. 7.21 illustrates the slight degradation of the ISS on increasing CNT diameter. As the diameter increases, the ISS decreases until it plateaus at approximately 25.9 MPa. Existing numerical works also predict an increase in the ISS with decreasing diameter [223,227,228]. This reduction demonstrates the advantage of using small diameter SWCNTs, due to their significantly higher ISS values when compared to larger diameter CNTs. The results of this study are summarized in Table 7-4.
Figure 7.20 Pull-out profiles for CNTs of varying diameter.

![Pull-out profiles for CNTs of varying diameter.](image)

Figure 7.21 Effect of CNT diameter on the interfacial shear strength.

![Effect of CNT diameter on the interfacial shear strength.](image)

Table 7-4 Details of the capping conditions considered.

<table>
<thead>
<tr>
<th>CNT Chirality</th>
<th>CNT Diameter (nm)</th>
<th>Peak Pull-out Force (nN)</th>
<th>$\tau_{\text{ISS}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5,5)</td>
<td>0.678</td>
<td>0.310</td>
<td>34.656</td>
</tr>
<tr>
<td>(8,8)</td>
<td>1.085</td>
<td>0.439</td>
<td>30.631</td>
</tr>
<tr>
<td>(12,12)</td>
<td>1.628</td>
<td>0.590</td>
<td>27.474</td>
</tr>
<tr>
<td>(15,15)</td>
<td>2.035</td>
<td>0.696</td>
<td>25.907</td>
</tr>
<tr>
<td>(18,18)</td>
<td>2.443</td>
<td>0.835</td>
<td>25.924</td>
</tr>
</tbody>
</table>
Effect of CNT and Polymer Capping

The previous studies examined the key parameters that influence the ISS for a non-bonded pull-out configuration where the CNT extended the same distance as the surrounding polymer. In all these cases, the pull-out profiles did not exhibit the initial characteristic peak in the pull-out force that is evident in experimental pull-out profiles. In this section, we illustrate the importance of accounting for the vdW interactions that occur at the base of the embedded CNT by incorporating both CNT caps and a polymeric region below the CNT. From this point forward, we refer to the polymeric region below the CNT as a polymeric end-cap. In this case, we consider a (10,10) armchair nanotube of length 4.42 nm embedded in the two-component DGEBA/TETA epoxy polymer representation. Five different capping conditions are considered and are summarized in Table 7-5 along with their schematic representations in Fig. 7.22.

<table>
<thead>
<tr>
<th>Capping Scenario</th>
<th>CNT Structure</th>
<th>Polymer End Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(10,10) open-ended</td>
<td>No polymeric end-cap</td>
</tr>
<tr>
<td>B</td>
<td>(10,10) open-ended</td>
<td>Polymeric end-cap</td>
</tr>
<tr>
<td>C</td>
<td>(10,10) capped</td>
<td>No polymeric end-cap</td>
</tr>
<tr>
<td>D</td>
<td>(10,10) capped</td>
<td>Un-conforming polymeric end-cap</td>
</tr>
<tr>
<td>E</td>
<td>(10,10) capped</td>
<td>Tight polymeric end-cap</td>
</tr>
</tbody>
</table>

Figure 7.22 Different CNT and polymer end capping conditions considered in the analysis.

A un-conforming polymeric end-cap refers to the case when the CNT is capped and the surrounding polymer does not entirely conform to its contour (Condition D). The interfacial thickness is slightly larger than the constant value of 0.34 nm used in our previous simulations near the base of the CNT. One should also note that the capped CNT geometries are offset from the open-ended geometries by a distance of approximately 0.27 nm. This is due to the curved shape of the CNT cap, which in turn reduces the effective length of the CNT. The tight
polymeric end-cap condition does conform to the CNT’s capped contour (Condition E). The polymer matrix entirely surrounds the CNT with a constant interfacial thickness of 0.34 nm. The most notable difference between these two scenarios is that the magnitudes of the vdW forces acting at the base of the CNT in the un-conforming condition are reduced due to the larger separation distances between the polymer and CNT atoms.

An initial comparison of the pull-out profiles for all five capping conditions is shown in Fig. 7.23 while a summary of the pull-out results for each condition is provided in Table 7-6. Examining the pull-out profiles highlights the significant effect that the capping condition can have on the pull-out characteristics. The most notable difference is the initial peaks evident in the pull-out profiles for Conditions B and E. These peaks arise from the added vdW interactions between the polymer and CNT atoms at the base of the nanotube when considering tight polymeric end-caps. Figure 7.24 illustrates the additional vdW forces that arise from these capping conditions which appose the applied pull-out force. A capped CNT with a tight polymeric end-cap (Condition E) has a peak pull-out force 2.85 times larger than the base condition A where neither a CNT cap nor a polymeric end-cap were considered. This results in a 16% increase in the energy required to pull out the CNT from the surrounding polymer (for a 4.42 nm CNT). The additional vdW interactions that arise from the added CNT and polymer atoms significantly improve the peak pull-out force and produce profiles characteristic of those observed in experiments. One might expect a similar result for Condition D, however, the peak pull-out force for this condition deviates by only 0.09% from the baseline condition. This is due to the larger interfacial thickness near the base which serves to reduce the magnitude of the vdW forces in that region. In addition, the capped CNT with no polymeric end-cap (Condition C) does not seem to deviate much from the baseline. As such, we can conclude that CNT caps do not significantly affect the magnitude of the pull-out force unless fully surrounded by the polymer matrix such that the additional atoms are capable of participating in these interactions. In support of these findings, Li et al. [223] investigated the pull-out force for a CNT embedded in polymer matrix via MD. Two cases were considered, an open-ended CNT and a capped CNT both fully embedded in the polymer. They observed a significantly higher pull-out force for a capped CNT than that of the corresponding open-ended CNT. These findings imply a significant contribution from the CNT cap to the interfacial properties of CNT-reinforced nanocomposites.
Figure 7.23 Pull-out profiles for capping conditions A through E.

Table 7-6 Pull-out results for different capping conditions.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.61E-10</td>
<td>-</td>
<td>5.06E-10</td>
<td>-</td>
<td>2.02E-09</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>7.73E-10</td>
<td>37.81%</td>
<td>5.14E-10</td>
<td>1.52%</td>
<td>2.22E-09</td>
<td>9.51%</td>
</tr>
<tr>
<td>C</td>
<td>5.57E-10</td>
<td>-0.72%</td>
<td>5.09E-10</td>
<td>0.60%</td>
<td>2.00E-09</td>
<td>-1.05%</td>
</tr>
<tr>
<td>D</td>
<td>5.61E-10</td>
<td>0.09%</td>
<td>5.11E-10</td>
<td>0.93%</td>
<td>2.07E-09</td>
<td>2.19%</td>
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<tr>
<td>E</td>
<td>1.60E-09</td>
<td>184.83%</td>
<td>5.10E-10</td>
<td>0.63%</td>
<td>2.36E-09</td>
<td>16.36%</td>
</tr>
</tbody>
</table>

Figure 7.24 Two dimensional schematic depiction of the cumulative resultant vdW forces along the length and base of a CNT during the pull-out process.
Effect of Covalent Bond Density

In the previous section, we illustrated the importance of accounting for the vdW interactions that occur at the base of the embedded CNT and how those interactions can significantly influence the predicted pull-out profiles and produce the sharp initial peaks evident in most experimental measurements. Here, we illustrate how interfacial modification via chemical bond formation can produce a similar response in the predicted pull-out profiles. In many cases, the chemical crosslinks between a CNT and polymer chain that arise from a functionalization treatment consist of functional units that are made up of several atoms with defined bond lengths. Figure 7.25 depicts the structure of some common functional units used in the molecular dynamic analysis of Zheng et al. [112]. Crosslinks have also been known to form only at defect sites in the walls or at the capped ends of the CNT where the bonding structure of the carbon atoms has been disturbed [229,230]. Clearly, the exact bonding structure and morphology of the crosslink unit is a complex entity on its own which depends on the polymer system and CNT structure considered and requires molecular dynamic analysis to model appropriately. However, the intent of this work is to illustrate the effect of crosslinking on the peak pull-out force which is largely dominated by the magnitude of the potential. In this case, a small percentage of covalent C-C bonds will be included in the interface description and modeled using the stretching component of the Modified Morse potential. The Modified Morse potential is well suited to model strong covalent bonds between carbon atoms and exhibits a peak force that exceeds that of the LJ potential by three orders of magnitude. It is expected that even a small percentage of covalent bonds acting as chemical crosslinks at the interface will drastically increase the peak pullout force and resulting ISS. Three cases with varying covalent bond densities will be considered, namely, 0.0%, 0.5%, 1.0% and 5.0%. The bond density refers to the number of atoms in the CNT that form covalent crosslinks with the surrounding polymer. The covalent bonds will be randomly distributed throughout the interface using anchoring points or, equivalently, polymer nodes located at a radial distance of 0.1421 nm away from the wall of the CNT. This distance corresponds to the equilibrium separation distance of the Modified Morse potential. Figure 7.26 depicts a 6.60 nm CNT with a 5.0% chemical bond density. In an experimental setting, the pull-out process occurs rapidly which allows limited time for new chemical bonds to form across the interface. Therefore, the chemical bonds in the present analysis are not regenerative. This implies that as the CNT is pulled out from within the surrounding polymer and the chemical bond exceeds its cutoff distance (2.5r_0 = 3.55 nm), the chemical interaction between those atoms is
simply terminated and a new bond is not permitted to form with a polymer atom that may fall within the allowable separation distance.

Figure 7.25 Atomic structure of functional groups considered in the MD analysis of Zheng et al. (From Ref. [112]).

Figure 7.26 A CNT with a 5.0% chemical bond density.

Figure 7.27 shows the predicted pull-out profiles for all four bond densities for a CNT of 6.60 nm in length. The figure clearly indicates that for all cases involving covalent bonds the peak
pull-out force is substantially increased and occurs during the initial stages of loading after which the pull-out force decreases to a nearly zero value. The inset in the figure illustrates that the pull-out profiles still exhibit the characteristic force oscillations once the covalent bonds have been broken.

Table 7-7 summarizes the results of this analysis and highlights the positive improvement in the average ISS for all three covalently bonded cases. For the case involving just 0.1% covalent bond density we see an increase of approximately 285% in the average ISS and an increase of nearly 3500% for a 5% covalent bond density. These results are supported by existing numerical works. For example Zheng et al. [112] used both molecular mechanics and MD to study the effect of chemical functionalization on the interfacial bonding characteristics of a SWCNT embedded in a PE matrix. They investigated the effect of several different functional groups and found that the ISS can improve by as much as 1700% for cases involving 5% of the carbon atoms in the CNT. These results clearly demonstrate the ability to improve the strength of CNT epoxy interfaces through interfacial modification and also provides an explanation for the discrepancies observed between experimental measurements and previous numerical predictions.

It should be noted that the magnitude of the peak pull-out force is largely governed by the number of covalent bonds considered but also by the initial separation distance of the atoms participating in the bond. This separation distance dictates the level of straining in the bond. For the current simulations this distance was taken to be equal to the equilibrium separation distance of the Modified Morse potential which produces the largest pull-out force. For illustrative purposes, Fig. 7.28 shows the initial pull-out response for the cases where the anchoring points have been displaced an additional 0.03 nm which corresponds to a 20% initial strain in the covalent bond. The pull-out curves are only extended to a 1.0 nm pull-out displacement and exhibit the same characteristic profiles, however, the peak pull-out forces show a substantial reduction in magnitude.
Figure 7.27 Pull-out profiles for cases involving varied covalent bond densities.

Figure 7.28 Pull-out profiles for cases involving varied covalent bond densities with a 20% prescribed initial strain.

Table 7-7 Pull-out results for varied covalent bond densities.

<table>
<thead>
<tr>
<th>Crosslink %</th>
<th>Peak Pull-out Force (nN)</th>
<th>Average ISS (MPa)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.67</td>
<td>20.5</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>44.46</td>
<td>79.1</td>
<td>285.1</td>
</tr>
<tr>
<td>1.0</td>
<td>89.19</td>
<td>134.4</td>
<td>554.5</td>
</tr>
<tr>
<td>5.0</td>
<td>224.30</td>
<td>736.3</td>
<td>3486.6</td>
</tr>
</tbody>
</table>
7.1.4 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, \( \alpha \). Here we adopt the Mori-Tanaka micromechanical modeling method as described in Section 5.2. The experimental program of this thesis only considers a randomly orientated dispersion of CNTs in the adhesive matrix. In fact, Fig. 7.29 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.

![Image](image1.png)

Figure 7.29 STEM micrograph of a nano-reinforced adhesive at 1.0 wt% CNT loading. The arrows denote the individual CNTs emanating from the surface.

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. 7.30 and 7.31, 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 [231] 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. 7.32 and 7.33, respectively. Yu et al. [232] 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. 7.34 and 7.35, 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 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. 7.36 and 7.37. Comparable trends were observed in the works of Odegard et al. [140] 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 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. Figure 7.30 demonstrates that anomaly 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.
Figure 7.30  Effect of CNT concentration on the longitudinal Young's modulus of nano-reinforced adhesives containing aligned CNTs.

Figure 7.31  Effect of CNT concentration on the transverse Young's modulus of nano-reinforced adhesives containing aligned CNTs.
Figure 7.32 Effect of CNT aspect ratio on the longitudinal Young’s modulus of nano-reinforced adhesives containing aligned CNTs.

Figure 7.33 Effect of CNT aspect ratio on the transverse Young’s modulus of nano-reinforced adhesives containing aligned CNTs.
Figure 7.34 Effect of CNT concentration on longitudinal shear modulus of nano-reinforced adhesives containing aligned CNTs.

Figure 7.35 Effect of CNT concentration on the transverse shear modulus of nano-reinforced adhesives containing aligned CNTs.
Figures 7.36 and 7.37 show the effect of CNT aspect ratio on the longitudinal shear modulus of nano-reinforced adhesives containing aligned CNTs.

Figures 7.38 and 7.39 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. 7.40 and 7.41. Figures 7.42 and 7.43 compare Young’s modulus and the shear modulus for
nano-reinforced adhesives containing both aligned and randomly orientated CNTs for the case where $a = 100$, 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. [140].

Figure 7.38 Effect of CNT concentration on the Young’s modulus of nano-reinforced adhesives containing randomly orientated CNTs.

Figure 7.39 Effect of CNT concentration on the shear modulus of nano-reinforced adhesives containing randomly orientated CNTs.
Figure 7.40 Effect of CNT aspect ratio on Young’s modulus of nano-reinforced adhesives containing randomly orientated CNTs.

Figure 7.41 Effect of CNT aspect ratio on the shear modulus of nano-reinforced adhesives containing randomly orientated CNTs.
7.1.5 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 5.3. 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. 7.44. 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.

![Figure 7.44 STEM micrograph of an individual CNT.](image)

**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 [233]. 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. Figure 7.45 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. 7.46. 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. Figure 7.47 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 0.5wt%.

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. [233] 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. [194] 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 [234] while only 16 for the case of randomly orientated and aligned cylindrical fibers [235]. Given the above variance, it is clear that the optimal cell size is a function of a number of geometrical and material parameters.

**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 to 3.0 vol% in increments of 0.5 vol%. Figure 7.48 depicts the constitutive response for all the models while Figs. 7.49 and 7.50 plot Young’s modulus and the tensile strength over the concentrations considered, respectively. The constitutive responses show the same overall trend while Figs. 7.49 and 7.50 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. 7.49 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 as discussed in Section 5.2.3.
Figure 7.48 Constitutive response of nano-reinforced adhesives under tensile load for CNT concentrations spanning 0.0 to 3.0 wt%.

Figure 7.49 Effect of CNT concentration on Young’s modulus of nano-reinforced adhesives.
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. Figure 7.51 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. Clearly, such a model would require hefty computational resources and is outside the scope of this research.
7.2 Experimental Findings

In this section, we present the results of our experimental program as it relates to the improvement of the mechanical properties of nano-reinforced adhesives through the dispersion of CNTs. Specifically, we address and discuss the findings of the (i) dogbone tensile test, (ii) tensile button test, (iii) double lap shear test, and the (iv) double cantilever beam test. In addition, the effect of surface preparation methodology and bond-line thickness upon the tensile bond strength of adhesives is also presented. We also demonstrate the impact of introducing the PVP surfactant as a dispersion stabilizer and assess the quality of the CNT dispersion using STEM techniques. Test specimens with CNT concentrations that ranged from 0.0 to 3.0 wt% in increments of 0.5 wt% were considered for all the experiments except the DCB test which investigates a maximum concentration of 2.5 wt%. Each CNT concentration group used a total of 10 test samples. Furthermore, the results are presented for two material systems, namely, the adhesive dispersed with CNTs (CNT) and the adhesive dispersed with CNTs and PVP (CNT & PVP) where the surfactant was added in equal parts to the CNTs. In all cases, the data pertaining to the adhesive with CNTs is represented with a dashed black line while the adhesive with CNTs & PVP is represented with a solid black line.
7.2.1 Effect of Surface Preparation Methodology

Preparation of the substrate surfaces prior to adhesive bonding is a mandatory stage of the bonding process. This includes both the degreasing and abrading of the substrate surfaces. To correctly prepare the surface to be joined, all grease, oil and foreign particles should be removed. With most high performance adhesives this step is critical, since for good wetting, the adherend should have a higher surface tension than the adhesive [10]. Clean substrate surfaces enhance the formation of intermolecular and chemical bonding between the substrate and adhesive molecules [236]. All substrate surfaces in this test program were cleaned and degreased using an isopropanol solution.

Mechanical abrasion is the most widely applicable surface preparation technique, being suitable for most materials. Mechanical abrasion will remove weak boundary layers. It will also change the surface topography of the adherend, increasing the bondable surface area on a microscale. Furthermore, mechanical abrasion will enhance the adhesive's ability to wet the surface of the adherend. Abraded substrate surfaces provide improved bonding strength due to the interlocking of the adhesive material in the surfaces micro-voids [10,236].

Two substrate surface abrasion methodologies were considered and evaluated in the fabrication of the test specimens. These include (i) hand abraded surfaces using standard sand paper with varied degrees of grit, and (ii) controlled shot blasted surfaces using metallic shots of varied diameter. Surface profile measurements were conducted on 4 groups of varied shot and grit size from both surface abrasion methodologies using a 3D surface profiler to obtain an average $S_a$ value as a measure of the surface roughness. Each group contained 5 test specimens. The substrates were then bonded using the pure epoxy and the tensile bond strength of the samples was evaluated. Figure 7.52 plots the average tensile strength of the adhesive bonds over the average $S_a$ value for both surface abrasion methodologies considered. The surface roughness seems to have an insignificant effect on the average tensile strength of the bond for the hand abraded samples. However, the $S_a$ values only span a range of $0.7 – 5.0 \mu m$ due to the availability of coarser grit sand paper. The average tensile strength over all $S_a$ values for the hand abraded samples is a mere 7.8 MPa. The shot blasted samples, on the other hand, exhibit an increase in the average tensile bond strength with decreasing shot size and surface roughness to a maximum of 17.4 MPa at a $S_a$ value of 3.9 $\mu m$. Uehara and Sakurai [237] also investigated the
effect of substrate surface roughness on the tensile bond strength of epoxy adhesives. They considered aluminum substrates with varied degrees of surface roughness and found that the tensile bond strength peaked at low surface roughness values and subsequently degraded. An optimal surface roughness in the range from 3 to 6 μm $R_a$ was observed in their study. They also observed no significant effect of the surface roughness on both the shear and peel strength of the adhesive bond.

![Graph showing the influence of substrate surface roughness and preparation methodology on the tensile bond strength of adhesives.](image)

In order to understand the discrepancy in the tensile bond strength of the two surface abrasion methodologies, we examine their surface profiles. Figure 7.53 shows typical surface profile scans for samples from both preparation methodologies. The scans were taken over a 4 mm$^2$ square area. Figure 7.53 (a) shows a typical profile scan for the hand abraded samples. The etched patterns from the sand paper are clearly visible and seem to exhibit a degree of alignment in a preferential direction. Figure 7.53 (b) shows the surface profile for the shot blasted samples at a comparable $S_a$ value. In this case, the surface appears to be much more uniform and also lacks the random and pronounced surface cavities when compared to the hand abraded samples.

We attribute the increase in the tensile bond strength to the uniformity of the surface produced by the shot blasting. We also hypothesize that the chosen epoxy system lacks the appropriate viscosity to properly penetrate the distinct cavities present in the hand abraded samples which would ultimately reduce the total wetted area. Furthermore, the deep cavities present in the hand
abraded samples may serve to trap impurities even after cleaning of the surface which can also lead to a degradation of the tensile bond strength. For illustrative purposes we also include a surface profile scan for a shot blasted specimen at a higher $S_a$ value in Fig. 7.53 (c). The random cavities formed from the impact of the larger metallic shots are clearly evident. Again, we believe the deep cavities are responsible for the degradation of the tensile bond strength as they reduce the wetted area and can trap impurities.

Figure 7.53 Typical surface profile scans for (a) hand abraded, (b,c) shot blasted surface preparation methodologies.
7.2.2 Effect of Bond-Line Thickness

Bond-line thickness is one of the important factors to be considered in the design of a bonded joint. Most commonly used bond-line thicknesses range from about 0.2 to 0.5 mm [10,238,239]. Generally, one tries to have as thin an adhesive layer as possible without any chance of bond starvation. With thicker adhesive bond-lines, one runs the risk of incorporating higher void concentrations into the joint [238,239]. Furthermore, thicker bond-lines lead to additional cleavage stresses at the corner of the adhesive and adherend because it is difficult to keep the loads axial with a very thick bond-line. It should also be noted that adhesives are generally formulated to cure in thin sections. Thicker sections could change the curing properties and result in increased internal stresses and different physical properties than optimal. In order to maintain a uniform bond-line thickness and to study its effect on the tensile strength of the adhesive bond, we disperse a very small amount (~0.02 wt%) of glass beads in the pure epoxy prior to the bonding of the substrates. Here, we investigate glass beads that range from 0.1 to 0.4 mm in diameter and measure the true bond-line thickness using an optical microscope. Table 7-8 summarizes the findings and indicates that the 0.4 mm glass beads result in the strongest bond. In fact, little difference is observed for thicknesses above 0.2 mm. However, existing studies also suggest that optimum joint thicknesses are observed from 0.2 to 0.5 mm. For example, Naito et al. [240] evaluated both the tensile and shear strength of epoxy adhesives as a function of bond thickness. While no significant effect was observed in the shear strength for the range of thicknesses considered, the tensile strength showed a maximum at approximately 0.2 to 0.3 mm. The bond-line thickness also influences other important mechanical properties. For example, van Tooren et al. [239] investigated the effect of adhesive bond-line thickness on the strength of single lap joints both experimentally and numerically using a stress singularity model. They observed a maximum bond strength at a thickness of 0.5 mm. Bascom and colleagues [241] and then Kinloch & Shaw [242] used linear elastic fracture mechanics tests to characterize the crack propagation resistance of adhesive joints up to 3 mm thick. They found an optimum joint thickness around 0.5 mm, and postulated that there is competition between a constraint mechanism, due to the rigid substrates, at low thickness, resulting in high tensile stresses, and the amount of dissipation in the plastic zone which increases to a maximum then reduces at higher thickness. Given that we only evaluate the tensile bond strength as a function of bond-line
thickness, we take a conservative approach and select 0.4 mm as the bond-line thickness for the remainder of the experiments.

Table 7-8 Effect of bond-line thickness on the tensile bond strength of adhesives.

<table>
<thead>
<tr>
<th>Glass Bead Size (mm)</th>
<th>Bond-line Thickness (mm)</th>
<th>Tensile Bond Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.100</td>
<td>4.284</td>
</tr>
<tr>
<td>0.2</td>
<td>0.193</td>
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</tr>
<tr>
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<td>6.194</td>
</tr>
<tr>
<td>0.4</td>
<td>0.398</td>
<td>6.424</td>
</tr>
</tbody>
</table>

7.2.3 Dogbone Tensile Test

The dogbone tensile test was used to evaluate the constitutive response of the pure epoxy adhesive and the nano-reinforced adhesives. This test method allowed for the direct measurement of the Young’s modulus and the tensile strength of the adhesives considered. Figure 7.54 shows a typical load-displacement plot obtained through the dogbone tensile test as measured for one of the pure epoxy samples. It should be noted that prior to loading of the test specimens to fracture, the load was cycled in the elastic range up to a maximum load of 0.5 kN for a total of 10 cycles to relax the material and reduce large fluctuations in the measured Young’s modulus. Cross sectional measurements were made at three different locations along the length of each test specimen for an average cross sectional area.

![Figure 7.54 Typical load displacement plot obtained through dogbone tensile testing of nano-reinforced adhesives.](image)
Upon testing, each sample’s fracture surface was examined for voids and impurities that may have initiated premature failure. If these were present, the measurement was discarded. Figure 7.55 shows one such fracture surface where failure was initiated from the presence of a void or air pocket, while Fig. 7.56 shows mirror images of a ‘clean’ fracture surface with the point of initiation clearly indicated. As can be seen, fracture initiates from the edge of the specimen and propagates into the sample. The beach marks from the propagation of the crack are also evident.

![Fracture surface of a nano-reinforced adhesive dogbone test sample containing a void.](image1)

Figure 7.55 Fracture surface of a nano-reinforced adhesive dogbone test sample containing a void.

![Fracture surface of a ‘clean’ nano-reinforced adhesive dogbone test sample.](image2)

Figure 7.56 Fracture surface of a ‘clean’ nano-reinforced adhesive dogbone test sample.

Figure 7.57 shows the variation of the Young’s modulus of nano-reinforced adhesives as a function of the CNT concentration. The addition of CNTs produces an increase in the Young’s modulus for all concentrations and material systems considered. The largest increase of 25% was observed at a concentration of 1.5 wt% for the CNT & PVP system while the CNT system exhibited a maximum increase of 25% at a concentration of 2.0 wt%. For all concentrations the
CNT & PVP system showed larger or equivalent increases in the Young’s modulus over that of the CNT system. At CNT concentrations over 2.0 wt% the tensile modulus of nano-reinforced adhesives seems to begin to degrade.

![Graph showing Young's modulus vs CNT concentration](image)

*Figure 7.57 Influence of CNT concentration on the Young's modulus of nano-reinforced adhesives (error bars denote ± one coefficient of variation).*

Figure 7.58 shows the variation in the tensile strength of the nano-reinforced adhesives over the concentrations considered. The dispersion of CNTs in the adhesive produces an increase in the tensile strength for all concentrations and material systems considered. The tensile strength exhibits a gradual increase to a maximum of 25% at 1.5 wt% for both material systems and then begins to degrade. Again, the addition of PVP seems to improve the tensile strength of the nanocomposite over that of the CNT system. The experimental data pertaining to this test was statistically evaluated by the analysis of variance (ANOVA) method, as described in Appendix B. The results of the ANOVA analysis show that both Young’s modulus and the tensile strength can be claimed as statistically different with a 99% confidence level. Evidently, these results suggest that there exists a critical CNT concentration over which the strength and stiffness of the nano-reinforced adhesives begin to degrade. At this stage it is difficult to explain the reasoning but we hypothesize that it is due to the improper dispersion of CNTs at higher concentrations and their re-agglomeration. We can also conclude that the addition of PVP as a surfactant has a favorable effect on both the tensile strength and stiffness of the resulting nano-reinforced adhesive.
7.2.4 Tensile Button Test

The tensile button test was used to evaluate the tensile bond strength of the nano-reinforced SABs for varied CNT concentrations. Figure 7.59 shows a typical load-displacement plot obtained through this test method while Fig. 7.60 plots the tensile bond strength of the nano-reinforced SABs over the CNT concentrations considered. Again, we see that the tensile bond strength shows a similar trend, an initial increase to a maximum at a critical CNT concentration and then a subsequent degradation. The PVP & CNT material system outperforms the CNT system for nearly all CNT concentrations with a maximum increase of 90% at a CNT concentration of 1.0 wt%. The CNT system shows a maximum increase of 54% at a concentration of 1.5 wt%. Clearly, both material systems produce a substantial increase in the tensile bond strength of nano-reinforced adhesives. Again, the experimental data pertaining to this test was statistically evaluated by the ANOVA method. The results of the ANOVA analysis show that the tensile bond strength can be claimed as statistically different with a 99% confidence level.
Figure 7.59 Typical load-displacement measurement from tensile button testing of nano-reinforced SABs.

Figure 7.60 Influence of CNT concentration on tensile bond strength of nano-reinforced SABs (error bars denote ± one coefficient of variation).

The fracture surfaces of the tensile button specimens were also visually inspected for cohesive and interfacial failure. A purely cohesive failure is indicative of a stronger interface. In this case the crack propagates through the weaker adhesive. Interfacial failure, on the other hand, suggests that the adhesive is stronger than the interface between the substrate and adhesive. Figs. 7.61 to 7.63 show the fracture surfaces for three samples from test groups containing 0.5, 1.0 and 3.0 wt% CNTs. Samples from the 0.5 wt% test group show nearly a purely cohesive failure mode.
Samples from the 1.0 wt% test group begin to show a small percentage of interfacial failure indicative that the dispersed CNTs have reinforced the adhesive adequately enough to force the crack to propagate along the interface. Finally, the 3.0 wt% test group samples show substantial interfacial failure, again, suggesting that further reinforcement of the adhesive by the CNTs has taken place.

Figure 7.61 Fracture surfaces of nano-reinforced SABs with a 0.5 wt% CNT concentration. The fracture surfaces indicate a purely cohesive failure mode.
Figure 7.62 Fracture surfaces of nano-reinforced SABs with a 1.0 wt% CNT concentration. The fracture surfaces show a small amount of interfacial failure.
7.2.5 Double Lap Shear Test

The DLS test was used to evaluate the shear bond strength of the nano-reinforced SABs. A typical load-displacement plot from this test is shown in Fig. 7.64 while Fig. 7.65 plots the shear bond strength over the range of CNT concentrations considered. Again, we see the same general trends in the shear response of both material systems. The shear bond strength increases to a maximum at some critical CNT concentration and then begins to generally degrade. For the CNT & PVP material system the maximum increase of approximately 25% occurs at a CNT concentration of 1.0 wt%. At a concentration of 3.0 wt% the shear bond strength of nano-reinforced SABs has degraded to below that of the pure epoxy. The results of the ANOVA analysis show that the shear bond strength can be claimed as statistically different with a 90% confidence level. For the CNT system no significant change is observed. In fact, the shear bond strength seems to oscillate around the value of the pure epoxy and in some cases slightly below.
It seems as though the dispersion of CNTs alone show no significant effect on the shear bond strength of nano-reinforced SABs.

![Typical load-displacement plot for double lap shear test.](image1)

**Figure 7.64** Typical load-displacement plot for double lap shear test.

![Influence of CNT concentration on shear bond strength.](image2)

**Figure 7.65** Influence of CNT concentration on shear bond strength (error bars denote ± one coefficient of variation).

### 7.2.6 Fracture Toughness Testing

The interfacial predictions from Section 7.1.3 are in good agreement with those in the literature. Hence, an optimization of the CNT diameter and length will lead to higher nanocomposite toughness due to increased energy dissipation with increasing ISS. High values of the ISS will
yield better crack bridging capabilities and cause the crack paths to deflect since the interface cannot be broken easily. To demonstrate the advantages of the crack bridging and CNT pull-out toughening mechanisms we evaluate the fracture toughness of the newly developed CNTnano-reinforced SABs for varied CNT concentrations.

**Double Cantilever Beam Test Results**

The most widely used method of determining the Mode I interlaminar fracture toughness of a composite material is the DCB test. The method is based in linear-elastic fracture mechanics theory and calculates the strain energy release rate using the crack length, the applied load, load point displacement, and initial specimen width. The DCB test was used to characterize the critical strain energy release rate, $G_{IC}$, in Mode I of the nano-reinforced adhesives. A typical load-displacement measurement from this test is shown in Fig. 7.66. As the DCB specimen is loaded the delamination front begins to undergo a complex stress state at the tip of the crack. Upon further loading the crack advances and there is a sudden drop in the measured load. This general trend is repeated until the full delamination of the substrates. A characteristic trait of these specimens is the jigsaw-like profile where each tooth represents one advancement in the crack trajectory. The points of crack advancement are labeled alphabetically as points (a)-(f) in Fig. 7.66. The corresponding fracture surface of the DCB test specimen is shown in Fig. 7.67. Evident in the figure are a number of closely packed beach marks which correspond to the crack advancement points (a)-(f) in the previous load-displacement plot. Also labeled in the figure is the location of the pre-crack which was initiated by first impregnating a 13 µm Teflon insert into the adhesive bond and by then driving a wedge into the test specimen to further initiate a crack a distance of approximately 3-5 mm into the bond. The beach marks are slightly curved to one side. The curvature is normally a good indicator of mixed mode loading. However, in the present analysis, if the locations of the beach marks where within 5 mm of each other on other side of the DCB specimen the measurement was assumed to be entirely Mode I.
As mentioned in Section 6.2.4, the strain energy release rate was evaluated using the corrected beam theory method which incorporated a correction factor, $\Delta$, to account for any possible rotation at the delamination front. $\Delta$ was determined experimentally by generating a least squares plot of the cubic root of compliance over the crack length as shown in Fig. 7.68. In all cases, the correction factor did not exceed 8 mm.
In the DCB test, as the delamination grows from the insert, a resistance-type fracture behavior typically develops where the calculated $G_{IC}$ first increases monotonically, and then stabilizes with further delamination growth giving a final value of $G_{IC}$. In this test method, a resistance curve ($R$ curve) depicting $G_{IC}$ as a function of delamination length is generated to characterize the initiation and propagation of delamination in the unidirectional composite specimen as shown in Fig. 7.69. It should be noted that not all DCB test specimens displayed this monotonical characteristic. In some cases the measured $G_{IC}$ values oscillated around some constant value for all crack lengths. It is assumed that this was mainly a result of extensive pre-cracking whereby the initial crack length was too large to capture the initial rise in the $G_{IC}$ values. In this case, the measured $G_{IC}$ values were averaged to give the final $G_{IC}$. 

![Figure 7.68 Typical least squares plot of the cubic root of compliance for a nano-reinforced DCB test specimen.](image)
The load-displacement plot shown in Fig. 7.66 is characteristic of the purely cohesive failure mode evident in the fracture surface of the test specimen shown in Fig. 7.71. In this case, the delamination growth proceeds in a run-arrest manner whereby the delamination front jumps ahead abruptly. However, in the case of a purely interfacial failure, which was observed for some specimens in the higher CNT concentration groups, the delamination growth proceeds by a slow stable extension. In this case, the load-displacement plot resembles that shown in Fig. 7.70. The load increases until the crack begins to advance through the interface and propagate slowly causing a gradual reduction in the load giving rise to the relatively smooth profile. The corresponding fracture surface for this type of interfacial failure is shown in Fig. 7.71.
Figure 7.70 Load-displacement plot for a nano-reinforced DCB test specimen exhibiting purely interfacial failure.

Figure 7.71 Fracture surface of a nano-reinforced DCB test specimen exhibiting purely interfacial failure.

Figure 7.72 plots the measured critical strain energy release rate for only the CNT & PVP material system over a CNT concentration range of 0.0 to 2.5 wt%. The 3.0 wt% data points are omitted due to a lack of required materials to fully characterize that test group. Again, we see the same trend of an initial increase up to a maximum at some critical concentration and then a subsequent decrease to a value, in this case, well below that of the pure epoxy. The maximum increase of approximately 36% was observed at a CNT concentration of 1.0 wt%. At a concentration of 2.5 wt% the critical strain energy release rate has degraded to a value approximately 45% less than that of the pure epoxy. At this state we hypothesize that this degradation is due to the agglomeration of the CNTs at higher concentrations which in turn degrades the quality of the CNT dispersion. The results of the ANOVA analysis show that the
critical strain energy release rate can only be claimed as statistically different with an 80% confidence level.

![Graph showing the effect of CNT concentration on strain energy release rate](image)

Figure 7.72 Effect of CNT concentration on the strain energy release rate of nano-reinforced adhesives (error bars denote ± one coefficient of variation).

These results seem to suggest that the crack bridging and CNT pull-out toughening mechanisms do play a significant role in the toughening of the nano-reinforced adhesive. However, it is also speculated that the presence of agglomerates at higher CNT concentrations drastically reduce the materials toughness and ability to resist fracture. Figures 7.73 and 7.74 show SEM micrographs of a fracture surface from one of the nano-reinforced DCB specimens. In both figures, MWCNTs can clearly be seen emanating from the fracture surfaces providing evidence of their reinforcement. The exposed nanotube surfaces in Fig. 7.73 seem to support the idea that nanotube pullout and crack bridging both act as strengthening and toughening mechanisms in nano-reinforced SABs. Figure 7.74 shows an embedded MWCNT agglomerate approximately 1 µm in diameter embedded in the epoxy. The micrograph was taken from a specimen with 2.5 wt% CNT concentration. It is expected that these agglomerates are responsible for the subsequent degradation of the observed properties at higher CNT concentrations.
7.3 Comparison of Numerical Predictions and Experimental Findings

The results of our experimental measurements clearly suggest that there exists some critical CNT concentration in the vicinity of 1.0 to 1.5 wt% that produces a maximum increase in the observed mechanical properties. At concentrations exceeding this critical value, the properties begin to degrade, in some cases to a value below that of the pure epoxy. We also note that the experimentally observed increases in the measured mechanical properties fall short of our numerical and theoretical predictions. Figure 7.75 compares the experimental measurements of Young’s modulus as taken from the dogbone test to that of the analytical predictions using the Mori-Tanaka scheme for randomly orientated inclusions and the numerical predictions of the proposed hybrid MC-FEA model over the CNT concentrations considered. At a concentration of 0.5 wt% the measurements agree well with the predictions with only a slight underestimate of approximately 10% when compared to the proposed model. At a concentration of 1.0 wt% we see a difference of 40%. Finally, at the highest concentration of 3.0 wt% we see substantial difference of approximately 200%. Likewise, Fig. 7.76 compares the experimentally measured tensile strength of the nano-reinforced adhesive to that of the proposed hybrid model. Again, we see only a small difference of approximately 10% and 25% at CNT concentrations of 0.5 and 1.0 wt%, respectively. However, at the highest concentration of 3.0 wt% the difference again totals 200%. We hypothesis that this phenomena is mainly due to the agglomeration of the CNTs at concentrations exceeding this critical value. In order to understand this abnormality and
deviation from theory we investigate the microstructure of the nano-reinforced adhesive and make a visual assessment of the quality of the dispersion and also comment on how the processing methodology affects its rheological properties.

Figure 7.75 Comparison of predicted and measured Young’s modulus of nano-reinforced adhesives.

Figure 7.76 Comparison of predicted and measured tensile strength of nano-reinforced adhesives.
7.3.1 Dispersion Assessment

Advanced electron microscopy techniques were used to investigate the microstructure of the nano-reinforced adhesives containing varying concentrations of CNTs. Specifically, STEM micrographs were taken of the 1.0, 2.0 and 3.0 wt% PVP & CNT samples at high resolutions. The imaging samples were prepared by pouring the respective uncured nano-reinforced adhesives into a silicon TEM mold. Once fully cured, the samples were removed and sectioned into 100 nm thick slices using an ultramicrotome equipped with a diamond cutting blade. Once sectioned, the slices were deposited onto copper grids with ultrathin carbon support films of approximately 3 nm thickness. The copper grids were then placed within the STEM and the nanocomposite sections were examined using dark field image acquisition at an incident beam voltage of 30 kV and at magnifications in some cases exceeding 80,000 times.

It is important to note that imaging of non-conductive materials such as adhesives are an extremely challenging task. This is mainly due to a ‘charging’ effect whereby the imagining specimen develops a negative charge from the buildup of electrons from the incident beam [243,244]. Traditionally, SEM techniques required an electrically-conductive sample or continuous conductive surface film to allow incident electrons to be conducted away from the sample surface to ground. If electrons accumulate on a nonconductive surface, the charge buildup causes a divergence of the incident electron beam and degrades the SEM image. In addition, both CNTs and thermoset epoxies share a common carbon composition which makes contrasting difficult. In order to suppress these issues, an environmental SEM equipped with a STEM detector and beam deceleration capabilities was used. In essence, this device is tailored for these materials and also allows for the deceleration of the incident electron beam just prior to impact which reduces the number of electrons that buildup on the specimen surface thereby reducing specimen charging.

Figure 7.77 depicts STEM micrographs of the 1.0 wt% CNT & PVP samples at two different levels of magnification. Figure 7.77(a) shows the surface of the nano-reinforced adhesive specimen at a magnification of approximately 40,000 times. At this level, artifacts from the cutting process are clearly evident and take the form of parallel diagonal markings on the surface with varying degrees of contrast. The micrograph also shows clear evidence of individual CNTs
protruding from the surface in the form of whiskers. The CNTs are well dispersed within the adhesive matrix and there is no evidence of agglomeration. At a magnification of approximately 31,500 times, the artifacts and CNT whiskers are still apparent but we also note the presence of a small fraction of agglomerates that range in size but do not exceed 1.0 μm as shown in Fig. 7.77(b). This suggests that the ultrasonication treatment combined with the use of PVP as a dispersion stabilizer was successful in breaking up the initial CNT agglomerates as they were combined with the adhesive. However, while the majority of the CNTs are uniformly dispersed in the adhesive, the duration and intensity of the ultrasonication process was insufficient to fully break-up and disperse all the CNTs.

Figure 7.78 depicts STEM micrographs of the 2.0 wt% CNT & PVP samples at two different levels of magnification. Shown in Fig. 7.78(a) is the surface of the specimen at a magnification of approximately 50,000 times. Again, the CNTs are clearly visible and seem well dispersed in the surrounding matrix and in a greater population when compared to the 1.0 wt% CNT sample. However, CNT bundles approximately 1.5 μm in size are also evident and upon reducing the magnification we see that the size and number of agglomerates has also increased (Fig. 7.78(b)). Finally, Fig. 7.79 shows the micrographs for the 3.0 wt% CNT & PVP sample. Here we see the presence of a number of agglomerates that range in size with the largest nearly 5.0 μm in diameter. We also note that there is a reduced occurrence of individual CNTs in the adhesive. At a reduced magnification of 10,000 times, the largest observed agglomerate totals nearly 10.0 μm in diameter with smaller ones in the near proximity as shown in Fig. 7.79(b).
Figure 7.77 STEM micrographs of the 1.0 wt% CNT & PVP nano-reinforced adhesive at two levels of magnification.
Figure 7.78 STEM micrographs of the 2.0 wt% CNT & PVP nano-reinforced adhesive at two levels of magnification.
Figure 7.79 STEM micrographs of the 3.0 wt% CNT & PVP nano-reinforced adhesive at two levels of magnification.
7.3.2 Rheological Characterization

The STEM micrographs observed in the previous section support our initial hypothesis of CNT agglomerates present in the nano-reinforced adhesives particularly at higher CNT concentrations. This seems to suggest that the ultrasonication treatment is not 100% successful in homogeneously dispersing all the initial CNT agglomerates. However, the experiment data does show an initial increase in the measured mechanical properties at lower concentrations. To explain this phenomenon, we present some rheological details that have been observed during the processing stages of the nano-reinforced adhesive. Specifically, we comment on how the dispersion of CNTs influences the viscosity of the base resin and thus the effectiveness of the ultrasonication treatment.

Recall, in our dispersion methodology outlined in Section 6.1.2 the CNTs were dispersed into the base resin using the ultrasonication treatment which was then subsequently cooled to room temperature before being mixed with the hardening agent. The base resin was first heated prior to dispersion to reduce its viscosity from 5.6 to 0.025 Pa·s. The ultrasonication treatment induces localized heating of the base resin even at low intensities which caused the base resin solutions to maintain their temperature of 100ºC even after treatment. During the ultrasonication process it was visibly and intuitively noticed that the viscosity of the base resin was increasing with CNT concentration. At concentrations below 1.0 wt% the solutions were capable of flow even after extended periods of sonication. The solutions would mix naturally and still maintain a fluid-like behaviour. At CNT concentrations exceeding 1.0 wt% processing of the material became difficult. The solutions would exhibit a whipped-cream-like consistency and the beaker containing the solution would have to be shifted in position in order to prevent a build-up of the material away from the ultrasonication horn. Degassing of the material prior to curing also became extremely challenging leading to trapped air in the final product. Therefore, viscosity measurements of the pure base resin and nano-reinforced base resins were taken using a Texas Instruments AR2000 rheometer equipped with an environmental test chamber at 100ºC to further elucidate on the rheological behaviour. The test setup utilized a 40 mm diameter steel cone with a 2º draft angle. One sample from each concentration group was tested with an average of 20 data points recorded over the shear rate range.
A typical viscosity measurement is shown in Fig. 7.80 which plots the viscosity over the shear rate with the steady state value denoted by a dashed line as was recorded for one of the 2.5 wt% samples. The other measurements exhibit similar trends of an initial decay in the viscosity followed by a slight oscillation around the steady-state value. Figure 7.81 plots the viscosity over the range of CNT concentrations considered. The viscosity exhibits an initial increase and then seems to reach a constant value in the range of 0.15 Pa·s at CNT concentrations exceeding 1.5 wt% which is comparable to the viscosity of common yogurts. Ideally, the viscosity would continue to increase with increasing CNT concentration [78,79]. However, the chart indicates that the solution has become saturated at this critical concentration. This suggests that the ultrasonication technique has lost its effectiveness beyond this viscosity value which is further supported by the micrographs of the previous section.

![Figure 7.80](image)

Figure 7.80 Typical viscosity measurement of nano-reinforced adhesives containing 2.5 wt% CNTs. The dashed line denotes the steady state value.
The ultrasonication technique operates on the principle of inertial cavitation whereby the horn oscillates producing high frequency sound waves causing the formation and subsequent implosion of voids which generate the necessary shear forces. These results suggest that through the dispersion of CNTs the viscosity of the resin increases to a critical value at which point the oscillations of the horn become insufficient in the further dispersion of the CNTs. At this stage, the resin has too great a resistance to the flow and shear of neighbouring polymer chains due to an interlocking and entanglement effect created by the presence of the CNTs and the subsequent increase in their intermolecular interactions. In fact, it is thought that the CNTs cause the microstructure to resemble that of a web-of-yarns. These results indicate that the molecular movement of the epoxy is significantly restricted as more of the CNTs’ surfaces become wetted by the adhesive thus limiting the effectiveness of the ultrasonication treatment at higher CNT concentrations. The processing was found to be much more difficult with increasing CNT concentration, as the densely packed tubes increased the viscosity of the resin due to an increase in their intermolecular interactions. The further addition of CNTs at concentration above 1.5 wt% simply leads to a build-up of their presence in the form of large agglomerates which compromises their reinforcement effect in the adhesive.

It is suggested that in order to circumvent this problem, a higher sonication intensity or duration is required. However, a higher intensity may lead to the burning of the polymer molecules due to the localized heating effect and longer sonication times typically result in the fragmentation of
the CNTs thus leading to smaller aspect ratios and reduced reinforcement. Alternatively, a lower viscosity medium may be required to fully utilize the ultrasonication processing methodology at higher CNT concentrations. It is also suggested to use additional mechanical dispersion techniques in conjunction with ultrasonication. For example, the calandering approach has been shown to be a very effective dispersion technique for high viscosity systems [73,75]. Lastly, a potential solution might involve using a low viscosity solvent such as ethanol to transfer the dispersed CNTs into the epoxy resin. The ethanol solution could then be heated to moderate temperature of 80°C to evaporate the ethanol leaving only the CNTs dispersed in the base resin mixture which would then be combined with the hardening agent.
Chapter 8
Conclusions and Future Work

Summary: In this final chapter, we provide a general summary of the principal conclusions of this work and outline the original contributions of the thesis. Furthermore, we discuss the limitations of the work and provide a brief description of the key areas that would benefit from additional efforts related to the contents of this thesis.

8.1 General Conclusions

In this thesis, a novel numerical approach to the characterization of nano-reinforced structural aerospace adhesives is presented. The numerical work is further supported by extensive experimental efforts into the determination of the influence of the dispersion of CNTs upon the mechanical properties of the newly developed nano-reinforced adhesives.

8.1.1 Multiscale Modeling of Nano-Reinforced SABs

A novel multiscale modeling technique that integrates governing atomistic constitutive laws in a continuum framework is developed for the characterization of nano-reinforced SABs. 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. Fundamental to the proposed concept is the notion that atomic bonds between two atoms act like load-bearing continuum elements, whereas individual atoms act as nodes of the related structure. MD interatomic potentials are used to derive the constitutive behavior of the finite elements thereby reducing the computational complexity of the problem while maintaining a comparable level of accuracy. In this way, an atomistically modified structural mechanics approach is adopted to treat the nanoscale problem. Appropriate formulations are developed to allow for the ABC modelling of nano-reinforced SABs on the basis of a nanoscale RVE that accounts for the nonlinear behaviour of its constituents; namely, the reinforcing carbon nanotube, the surrounding adhesive and their interface. 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 tensile loads. Based on this ABC approach, the constitutive response of individual CNTs are investigated under both tensile and torsional loads. The results confirm the original hypotheses that these nanoscale fibers exhibit extremely high strength and stiffness. The interfacial characteristics between the CNT and surrounding adhesive are also quantified through simulating a pull-out experiment. These studies offer insight into how the various parameters influence the ISS and further highlight the importance of accounting for the morphological conditions surrounding the embedded end of the nanotube and how they can be used to explain the discrepancies observed in existing experimental efforts. Furthermore, the studies are extended to emphasize the positive effect of chemically modifying the interface to further improve the load transfer at the interface. Finally, the bulk effective properties of the nanocomposite are predicted. These multiscale solutions indicate a substantial reinforcement effect from the homogeneous dispersion of CNTs.

8.1.2 Experimental Investigations of Nano-Reinforced SABs

This thesis extends the theoretical work by offering experimental insight into the mechanical properties of nano-reinforced structural adhesives. Two material systems are investigated to further elucidate on the effectiveness of using surfactants as a dispersion stabilizing agent, namely, a CNT material system which only contains dispersed MWCNTs in the adhesive and a CNT & PVP material system which also contains equal concentrations of polyvinylpyrrolidone to that of the MWCNT. Specifically, four key experiments are conducted; (i) dogbone testing, (ii) tensile button testing, (iii) double lap shear testing, and (iv) double cantilever beam testing. The results of the dogbone tests indicate an approximate improvement of 25% in both the tensile strength and stiffness of the nano-reinforced structural adhesives for both material systems. The tensile adhesive puck tests show an impressive 90% improvement in the tensile bond strength for the CNT & PVP system and a 54% improvement for the CNT system. These tests also suggest a cohesive failure mode at low CNT concentrations and a shift to interfacial failure at concentrations exceeding 1.0 wt%. The DLS tests show only a modest improvement of only 25% in the shear bond strength for the CNT & PVP system and no apparent change when only CNTs are used. Finally, the results of the DCB tests indicate an improvement of 36% in the critical strain energy release rate over that of the pure epoxy. Here, only the CNT & PVP system are evaluated. In all cases the CNT & PVP material system produced favourable increases over that of the CNT system. In addition to the abovementioned tests, attention is also given to the surface
preparation methodology and bondline thickness and their effect on the tensile strength of the nano-reinforced SABs. Of the two techniques considered, namely, hand abraded and shot blasted, the shot blasting surface preparation methodology producing low $S_a$ values results in the strongest bond which can is attributed to the uniformity of the surface and the lack of cavities which may serve to trap impurities and reduce the total wetted area.

8.1.3 Comparison of Numerical Predictions and Experimental Findings

The results of the experimental program clearly suggest that there exists some critical CNT concentration in the vicinity of 1.0 to 1.5 wt% that results in the largest improvement in the observed mechanical properties. At concentrations exceeding this critical value, the properties begin to degrade, in some cases to a value below that of the pure epoxy. We also note that the experimentally observed increases in the measured mechanical properties fall short of our numerical and theoretical predictions particularly at higher CNT concentrations. To explain this abnormality and deviation from theory we conduct investigations into the microstructure and rheological properties of the newly developed nano-reinforced adhesives. Specifically, advanced electron microscopy techniques are used to make a visual assessment of the quality of the CNT dispersion at CNT concentrations of 1.0, 2.0 and 3.0 wt%. These results indicate a relatively uniform and homogeneous dispersion at a CNT concentration of 1.0 wt%. However, the STEM micrographs also show the presence of large agglomerates at concentrations of 2.0 and 3.0 wt% which confirm our initial hypothesis of the mechanical degradation due to agglomerate formation. We also perform viscosity measurements on the nano-reinforced adhesives which indicate that the adopted ultrasonication dispersion methodology is only effective up to a CNT concentration of 1.5 wt% at which point the viscosity of the base resin has become saturated by the presence of CNTs which makes further processing extremely difficult. The increasing presence of CNTs and their intermolecular interactions restricts the molecular movement of the polymer chains thus limiting the ability of the ultrasonication horn to introduce the necessary shear forces. Potential remedies to the adopted dispersion methodology have also been presented.

8.2 Thesis Original Contributions

The main contributions of the current work can be summarized as follows:

1. Numerically investigated the constitutive response of individual CNTs and the interfacial characteristics between reinforcing CNT and surrounding adhesive using the ABC approach.
A key finding of these studies is the importance of accounting for the morphological conditions near the embedded end of the nanotube to better replicate experimental measurements.

2. Developed a novel multiscale model capable of predicting the mechanical behavior of nano-reinforced adhesives through the integration of atomistic and continuum scales. The model allowed for the prediction of the full nonlinear constitutive response of the nano-reinforced adhesives subject to tensile loads.

3. Investigated the influence of CNT concentration and aspect ratio upon the constitutive response of the nano-reinforced adhesives using the above multiscale modeling technique.

4. Successfully dispersed CNTs into structural adhesives using the ultrasonication technique. Further characterized the mechanical and fracture behavior of newly developed nano-reinforced SABs.

5. Identified a critical CNT concentration which resulted in a maximum increase in the observed mechanical properties. The critical concentration was shown to be a result of agglomeration arising from rheological changes to the material as evidenced by STEM analysis.

In addition to the abovementioned contributions, the current work has also resulted in a number of academic achievements. The work presented in this thesis has lead to the publication of 8 journal entries, 11 conference presentations and 5 distinctions. The exact details pertaining to these achievements are presented in Appendix C.

8.3 Future Work

The following areas are worthy of consideration in future research projects:

1. The model only considers uniformly distributed and randomly orientated straight CNTs of constant aspect ratio in the full constitutive response predictions. In order to better correlate the results to experimental measurements the model must be extended to consider agglomeration, CNT curvature, and preferential alignment of the CNTs.
2. Extend the model to investigate the bulk constitutive response for various degrees of agglomeration. Also investigate different modes of loading.

3. The model has tremendous potential in the field of structural health monitoring. CNT also exhibit extraordinary electrical conductivities and give rise to a percolation threshold when introduced in adhesives. Therefore, a direct extension of this model would be to allow for the prediction of electrical conductivity as a function of applied strain which could be used to characterize the electrical footprint of various damage modes.

4. Investigate additional dispersion methodologies that can be used in conjunction with the ultrasonication technique. Furthermore, additional tests on the use of surfactants as dispersing agents and stabilizers warrant attention.

5. The newly developed multiscale model requires considerable computational resources and this may cause difficulties in certain applications. Effort must be made to reduce the size of the model without sacrificing accuracy particularly for the cases involving high CNT concentrations and agglomeration.
References


Appendix A: Components of the Eshelby, $S_{ijkl}$, Tensor

For an ellipsoidal inclusion aligned along the $x_1$-axis with aspect ratio $\alpha = L/d$, the components of the Eshelby tensor are given as [185]:

\[
S_{1111} = \frac{1}{2(1-\nu_o)} \left\{ 1-2\nu_o + \frac{3\alpha^2 - 1}{\alpha^2 - 1} - \left[ 1-2\nu_o + \frac{3\alpha^2}{\alpha^2 - 1} \right] g \right\}
\]

\[
S_{2222} = S_{3333} = \frac{3}{8(1-\nu_o)} \frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4(1-\nu_o)} \left[ 1-2\nu_o - \frac{9}{4(\alpha^2 - 1)} \right] g
\]

\[
S_{2233} = S_{3322} = \frac{1}{4(1-\nu_o)} \left\{ \frac{\alpha^2}{2(\alpha^2 - 1)} + \left[ 1-2\nu_o + \frac{3}{4(\alpha^2 - 1)} \right] g \right\}
\]

\[
S_{2211} = S_{3311} = -\frac{1}{2(1-\nu_o)} \frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4(1-\nu_o)} \left[ \frac{3\alpha^2}{\alpha^2 - 1} - (1-2\nu_o) \right] g
\]

\[
S_{1122} = S_{1133} = -\frac{1}{2(1-\nu_o)} \left[ 1-2\nu_o + \frac{1}{\alpha^2 - 1} \right] + \frac{1}{2(1-\nu_o)} \left[ 1-2\nu_o + \frac{3}{2(\alpha^2 - 1)} \right] g
\]

\[
S_{3323} = S_{3322} = \frac{1}{4(1-\nu_o)} \left\{ \frac{\alpha^2}{2(\alpha^2 - 1)} + \left[ 1-2\nu_o + \frac{3}{4(\alpha^2 - 1)} \right] g \right\}
\]

\[
S_{1313} = S_{1212} = \frac{1}{4(1-\nu_o)} \left\{ 1-2\nu_o - \frac{\alpha^2 + 1}{\alpha^2 - 1} - \frac{1}{2} \left[ 1-2\nu_o + \frac{3(\alpha^2 + 1)}{\alpha^2 - 1} \right] g \right\}
\]

where $\nu_o$ is the Poisson ratio of the matrix, and

\[
g = \frac{\alpha}{(\alpha^2 - 1)^{3/2}} \left\{ \alpha \left( \alpha^2 - 1 \right)^{1/2} - \cosh^{-1} \alpha \right\}
\]

\[
= \frac{\alpha}{(1-\alpha^2)^{3/2}} \left\{ \cos^{-1} \alpha - \alpha \left( 1 - \alpha^2 \right)^{1/2} \right\}
\]

(82)

for prolate and oblate shaped inclusion cross-sections, respectively. All other components of the Eshelby tensor are zero.
Appendix B: Analysis of Variance Statistical Method

The analysis of variance (ANOVA) statistical method was used where appropriate to evaluate the heterogeneity of experimental measurements of the same test. The details of the one-way ANOVA analysis are provided below:

Assume the test has ‘a’ different levels of a single factor (CNT concentration) that is to be compared and let us refer to them as ‘treatments’. The experimental observations or measurements may be described by the linear statistical model:

\[
Y_{ij} = \mu + \tau_i + \epsilon_{ij} \quad \text{for } i = 1,2,...,a \quad j = 1,2,...,n
\]

where \(Y_{ij}\) is a random variable denoting the \(j\)th observation taken under treatment \(i\), \(\mu\) is the overall mean, \(\tau_i\) is the effect of the \(i\)th level of the factor, and \(\epsilon_{ij}\) is a random error component having a normal distribution with mean zero and variance equal to the standard deviation. The hypotheses to be tested are:

\[
H_0 : \tau_1 = \tau_2 = ... = \tau_a = 0
\]

\[
H_1 : \tau \neq 0 \text{ for at least one}
\]

Let \(y_i\) represent the total of the observations under the \(i\)th treatment and \(\bar{y}_i\) represent the average of the observations under the \(i\)th treatment. Similarly, let \(y_{..}\) represent the grand total of all observations and \(\bar{y}_{..}\) represent the grand mean of all observations. Expressed mathematically,

\[
y_{i.} = \sum_{j=1}^{n} y_{ij} \quad \bar{y}_{i.} = y_{i.} / n \quad i = 1,2,...,a
\]

\[
y_{..} = \sum_{i=1}^{a} \sum_{j=1}^{n} y_{ij} \quad \bar{y}_{..} = y_{..} / N
\]

where \(N = an\) is the total number of observations and the “dot” subscript notation implies summation over the subscript that it replaces.

The sum of squares identity for the proposed analysis is:


\[ SS_T = SS_{Treatment} + SS_E \]  

(86)

where

\[ SS_T = \sum_{i=1}^{a} \sum_{j=1}^{a} (y_{ij} - \bar{y}_{..})^2 \]  

(87)

\[ SS_{Treatment} = n \sum_{i=1}^{a} (\bar{y}_i - \bar{y}_{..})^2 \]  

(88)

\[ SS_E = \sum_{i=1}^{a} \sum_{j=1}^{n} (y_{ij} - \bar{y}_{i.})^2 \]  

(89)

The mean squares for treatments is:

\[ MS_{Treatment} = SS_{Treatment} / (a-1) \]  

(90)

and the error mean square is defined as:

\[ MS_E = SS_E / [a(n-1)] \]  

(91)

Finally, it can be shown that if the null hypothesis \( H_0 \) is true, the ratio

\[ F_o = \frac{MS_{Treatment} / (a-1)}{MS_E / [a(n-1)]} = \frac{MS_{Treatment}}{MS_E} \]  

(92)

has an F-distribution with \( a-1 \) and \( a(n-1) \) degrees of freedom. The null hypothesis is rejected at the \( \alpha \) level of significance if \( f_o > f_{\alpha,a-1,a(n-1)} \). The above calculations are displayed in an ANOVA table. Table B-1 and B-2 summarize the results of the analysis for Young’s modulus and tensile strength, respectively. Table B-3 and B-4 contain the results of the analysis for the tensile bond strength and shear bond strength. Finally, the ANOVA for the critical energy release rates of the DCB test are listed in Table B-5.
Appendix C: Academic Achievements Related to This Work

Journal Publications:


Conferences & Workshops:

- NSTI Nanotechnology Conference and Exposition, Santa Clara, California, June 2012.
- Adhesive and Sealant Convention, Denver, Colorado, April 2012.
- GMSI-BK21MAE Summer Camp, Seoul, South Korea, July 2011.
- NSTI Nanotechnology Conference and Exposition, Boston, Massachusetts, June 2011.
• MIE Research Symposium, Toronto, Canada, May 2011.
• ASME International Mechanical Engineering Exposition, Vancouver, Canada, November 2010.
• NSTI Nanotechnology Conference and Exposition, Anaheim, California, June 2010.
• COSM-UT² 2010 Graduate Student Workshop, Tokyo, Japan, May 2010.
• 3rd International Conference on Integrity, Reliability and Failure, Porto, Portugal, July 2009.
• NSTI Nanotechnology Conference and Exposition, Houston, Texas, May 2009.
• ASME International Mechanical Engineering Exposition, Boston, Massachusetts, November 2008.

Awards & Distinctions:

• MIE Student Travel Grant – April 2012
• 3rd Place in Innovation - July 2011: Awarded at the GMSI-BK21MAE Summer Camp
• Best Oral Presentation - May 2011: Awarded at the MIE Research Symposium
• NSERC - PGSD – 2010/2011/2012
• University of Toronto Nanotechnology Network Award – November 2009
• OGSST Dupont Canada Award – September 2009
• Lockheed Martin Special Innovation Scholarship – May 2009: Awarded at NSTI NanoTech in Houston
• Innovation Award – November 2008: Awarded at the ASME IMECE in Boston