Multiscale Modeling of Multifunctional Carbon Nanotube Reinforced Polymer Composites

by

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Abstract

In this thesis, novel multiscale modeling techniques have been successfully developed to study multifunctional nanocomposite polymeric materials. Interfacial, mechanical, electrical, and piezoresistive properties of carbon nanotube (CNT)-reinforced polymer composites were investigated using molecular dynamics (MD), micromechanics, and coupled electromechanical modeling techniques. Additionally, scanning electron microscopy was used to determine the morphology and dispersion state of a typical CNT-epoxy composite. Based on these measurements, realistic nanocomposite structures were modeled using representative volume elements (RVEs) reinforced by CNTs with different aspect ratios, curvatures, orientations, alignment angles, and bundle sizes. At the nanoscale level, the interfacial shear strength was determined via pull-out MD simulations. Additionally, the stiffness constants of a pure polymer, pristine and defective CNTs, and an effective fiber consisting of a CNT and a surrounding layer of polymeric chains were determined using the constant-strain energy minimization method. The obtained atomistic mechanical properties of the composite constituents were then scaled up using Mori-Tanaka micromechanical scheme.

Monte Carlo simulations were conducted to determine the percolation and electrical conductivity of RVEs containing randomly dispersed CNTs. An advanced search algorithm was developed to
identify percolating CNT networks and transform them into an equivalent electrical circuit formed from intrinsic and tunneling resistances. A solver based on the modified nodal analysis technique was then developed to calculate the effective conductivity of the RVE. Finally, the electrical model was coupled with a three-dimensional finite element model of the RVE to determine the coupled electromechanical behavior of the composite under tensile, compressive, and shear loads from the resistance-strain relationship.

The outcome of the developed modeling approach revealed that: the elastic modulus of a nanocomposite reinforced with well-dispersed straight CNTs was found to increase almost linearly with the increase of their volume fraction and double at CNT volume fraction of 5.0%; the combined effect of CNT waviness and agglomeration results in a significant reduction in the bulk properties of the nanocomposite; CNTs with grain boundaries perpendicular to the tube axis experience 60% reduction in its mechanical strength; and the nanocomposite gauge factor can reach up to 3.95 and is sensitive to loading direction and CNT concentration.
DEDICATIONS

To my wife Doha  
My love for you shall live forever

To my children Iyad and Rosanne  
For the happiness they brought to my life

To my Mom, Dad, brother and sisters  
For their continuous support and encouragement
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Dietrich Bonhoeffer said, “In normal life we hardly realize how much more we receive than we give, and life cannot be rich without such gratitude. It is so easy to overestimate the importance of our own achievements compared with what we owe to the help of others.” This important milestone in my life would have been impossible without the love, guidance, and support from my family and friends.

I owe forever my sincerest gratitude to my thesis supervisor, Prof. Shaker Meguid, for his patience, guidance, engagement, encouragement, financial help, and for believing in my potentials. His scientific integrity and intellect in research have fueled my intellectual and personal growth.

During my studies at the University of Toronto, I have been privileged to work with top researchers in the solid mechanics filed. A special thank you goes to Dr. Shailesh Kundalwal and Dr. Nuwan Dewapriya with whom I had the chance to collaborate with. I would like to express my sincere gratitude to my current and previous colleagues at the MADL research group for providing a great work atmosphere and for helping me in various ways. They are Mohamed Hassan, Pieter Verberne, Prayers Roy, Jacob Wernik, Farooq Al Jahwari, Lim Liang Ying, Mo Gabriel Shi, Rasool Moradi-Dastjerdi, Michael Chen, Sheldon Peng, Teng Cui, Brayden Ridley, and Valerie Meguid.

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CO-AUTHORSHIP AND LIST OF PUBLICATIONS

This is to certify that the work presented in this thesis was conducted by me, Ahmed Alian. Dr. Shaker Meguid is my thesis supervisor and a co-author of all papers included in this dissertation. He was instrumental in setting up the entire project and the ideas behind it. Dr. Shailesh Kundalwal is a co-author of papers 3, 7, and 8 that make up part of this thesis. He provided some limited input to the modeling and analysis phases of the research, and reviewed some aspects of the manuscripts prior to submission to Dr. Meguid for accurate proof reading and contribution to the technical content and validity of the hypotheses considered in the entire thesis. Dr. Sami El-Borgi is a co-author of paper 6. He provided some input to the analysis of results during my visit of Texas A&M university (Qatar) in 2015. I can testify that I conducted the analyses and prepared the initial drafts of all manuscripts. In addition, I conducted any additional work that seemed necessary, revised the manuscripts based on the suggestions of the co-authors, submitted the manuscripts for publication, and prepared final revisions as requested by external peer reviewers’ comments. In almost all the revisions, the reviewers acknowledged both the originality and importance of the work to the future of nanocomposites. This thesis is a compilation of my articles and book chapters that have been published during the tenure of my doctorate. However, it is important to note that for the sake of conciseness and focus, I have not included papers 2, 4, and 9 and book chapter 2.

BOOK CHAPTERS:


JOURNAL PAPERS:


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2. S.A. Meguid, A.R. Alian, Multiscale modeling of the elastic behaviour of a thermoset nanocomposite containing agglomerated and wavy CNTs, Engineering Mechanics Institute Conference (EMI2018), May 2018, MIT, Cambridge, MA, USA (*Invited*)


# TABLE OF CONTENTS

ABSTRACT ....................................................................................................................... ii
DEDICATIONS ...................................................................................................................... iv
ACKNOWLEDGEMENTS ....................................................................................................... v
CO-AUTHORSHIP AND LIST OF PUBLICATIONS ............................................................ vi
TABLE OF CONTENTS ....................................................................................................... viii
LIST OF TABLES ................................................................................................................. xiii
LIST OF FIGURES .............................................................................................................. xv
LIST OF APPENDICES ....................................................................................................... xxii
LIST OF ABBREVIATIONS AND SYMBOLS .................................................................. xxiii

Chapter 1. Introduction and Justification ........................................................................ 1
   1.1 Introduction .................................................................................................................. 1
   1.2 Justification for the study ......................................................................................... 4
   1.3 Objectives .................................................................................................................. 6
   1.4 Method of Approach ................................................................................................. 7
   1.5 Plan and Organization of Thesis ............................................................................... 10
   1.6 References ................................................................................................................. 11

Chapter 2. Literature Review .......................................................................................... 13
   2.1 Modeling and characterization of interfacial properties ........................................... 13
   2.2 Modeling and characterization of mechanical properties ......................................... 17
   2.3 Modeling of CNTs with grain boundaries ................................................................. 19
   2.4 Modeling and characterization of electrical properties ............................................. 21
   2.5 Modeling and characterization of electromechanical coupling ............................... 24
   2.6 References ................................................................................................................. 27

PART I Mechanical Properties of CNT-Reinforced Polymer Composites ........ 31

Chapter 3. Paper #1: Multiscale modelling of carbon nanotube epoxy composites .... 32
   3.1 Abstract ..................................................................................................................... 32
   3.2 Introduction ................................................................................................................. 33
   3.3 Multiscale Modeling Procedure ............................................................................... 36
      3.3.1 MD Simulations .................................................................................................. 36
      3.3.2 Micromechanics Model ...................................................................................... 46
3.4 Results and Discussion .............................................................................................................. 48
  3.4.1 Comparisons with Existing ABC Results .............................................................................. 48
  3.4.2 Effect of orientation and agglomeration of CNTs ................................................................. 49
3.5 Conclusions ..................................................................................................................................... 55
3.6 Acknowledgements ....................................................................................................................... 56
3.7 References ....................................................................................................................................... 56

Chapter 4. Paper #2: Multiscale modeling of the effect of waviness and agglomeration of CNTs on the elastic properties of nanocomposites .................................................................................................................. 58
4.1 Abstract ......................................................................................................................................... 58
4.2 Introduction ...................................................................................................................................... 59
4.3 Multiscale modeling ......................................................................................................................... 62
4.4 Molecular Dynamics Simulations .................................................................................................. 63
  4.4.1 Modeling of nanocomposite reinforced with wavy CNTs ......................................................... 63
  4.4.2 Modeling of Nanocomposite Reinforced with Agglomerated Wavy CNTs ................. 65
  4.4.3 Boundary Conditions ............................................................................................................... 67
  4.4.4 Molecular Dynamics Implementation ..................................................................................... 68
  4.4.5 Micromechanical Modeling ..................................................................................................... 68
4.5 Results and Discussion .................................................................................................................... 69
  4.5.1 MD Results and Nanoscale Level Properties .......................................................................... 69
  4.5.2 Micromechanics Results and Bulk Properties ......................................................................... 72
4.6 Conclusions ....................................................................................................................................... 78
4.7 Acknowledgements ........................................................................................................................ 79
4.8 References ....................................................................................................................................... 79

Chapter 5. Paper #3: Large-Scale Atomistic Simulations of CNT-Reinforced Thermoplastic Polymers ................................................................................................................................................. 81
5.1 Abstract ......................................................................................................................................... 81
5.2 Introduction ...................................................................................................................................... 82
5.3 Modeling Strategy ........................................................................................................................... 84
  5.3.1 Modeling of Reinforcing CNTs ................................................................................................. 85
  5.3.2 Modeling of CNT-Reinforced PE Composite ......................................................................... 87
  5.3.3 Development of RVEs with different CNT volume fractions ............................................... 88
  5.3.4 Development of RVEs with different CNTs bundle sizes ..................................................... 89
PART III Piezoresistive Properties of CNT-Reinforced Polymer Composites  163


9.1 Abstract.................................................................164
9.2 Introduction.............................................................165
9.3 Simulation Procedure..................................................168
9.4 Electrical Model ............................................................................................................. 169
9.5 Coupled Electromechanical Model ............................................................................... 173
9.6 Results and discussion ................................................................................................. 176
  9.6.1 Percolating and Conducting Networks ................................................................ 176
  9.6.2 Electromechanical Response ................................................................................. 179
9.7 Conclusions .................................................................................................................. 184
9.8 Acknowledgment .......................................................................................................... 185
9.9 References .................................................................................................................... 185
Chapter 10. Conclusions, Contributions and Future Work ............................................. 188
  10.1 Summary of Findings ............................................................................................... 188
    10.1.1 Atomistic Modeling of the Interfacial Properties .............................................. 188
    10.1.2 Multiscale Modeling of the Mechanical Properties ............................................. 189
    10.1.3 Large scale MD simulation of RVEs with Realistic Microstructures ............... 190
    10.1.4 Influence of grains boundaries on mechanical and fracture properties of CNTs  ................................................................................................................................. 190
    10.1.5 Coupled Electromechanical Modeling of Piezoresistive Properties ............. 191
  10.2 Thesis original contributions ...................................................................................... 192
  10.3 Future work .............................................................................................................. 193
Appendix 1: Basics of MD simulations ............................................................................. 194
Appendix 2: Eshelby Tensor in Micromechanical Model .................................................. 200
Appendix 3: Experimental Investigations ......................................................................... 201
LIST OF TABLES

Table 3-1 Elastic moduli of the epoxy material. .................................................................40
Table 3-2 Parameters used in the RVE. .............................................................................44
Table 3-3 Effective elastic coefficients of the RVEs and corresponding displacement fields. ..................................................................................................................45
Table 3-4 Material properties of the nanocomposite RVE containing either an individual CNT or its bundle........45
Table 4-1 Parameters used in the RVEs with wavy (5,5) SWCNTs of length 256 Å at ~1.8 vol %........64
Table 4-2 Details of the simulated RVEs with agglomerated wavy SWCNTs. .......................64
Table 4-3 Effective elastic coefficients of the RVEs and the corresponding displacement fields. ............69
Table 4-4 Effective elastic coefficients of the RVEs reinforced with well-dispersed (i.e. individual) wavy CNTs. 70
Table 4-5 Effective elastic coefficients of the RVEs reinforced with agglomerated wavy CNTs at 3.5 vol %. The waviness parameter, α, of the CNTs is 0.54.................................................................72
Table 5-1 Parameters of the SWCNTs used in the MD simulations. All CNTs are armchair with (5,5) chirality and 6.78 Å diameter ..................................................................................................86
Table 5-2 Details of the RVEs used in investigating the system size effect on the elastic properties of CNT-PE composite. All CNTs are armchair with (5,5) chirality, 131.0 Å length, and 6.78 Å diameter. The CNT volume fraction in all RVEs is 2.0%........................................................................................................................................88
Table 5-3 Details of the RVEs used in investigating the CNT volume fraction impact on the elastic properties. All CNTs are armchair with (5,5) chirality, 68.0 Å length, AR = 100, and 6.78 Å diameter. The side length of all RVEs is 122.5 Å ........................................................................................................................................89
Table 5-4 Details of the RVEs used in investigating the CNT agglomeration impact on the elastic properties. All CNTs are armchair with (5,5) chirality, 131.0 Å length, AR = 200, and 6.78 Å diameter. The CNT volume fraction in all RVEs is 3.0%. ........................................................................................................................................90
Table 5-5 Details of the RVEs used in the effect CNT morphology study. All CNTs are SWCNTs with chirality (5,5) and they represent 3.0 vol.% in total ................................................................................................91
Table 5-6 Effective stiffness constants of the RVEs and the corresponding displacement fields. ...............93
Table 5-7 The stiffness constants and the corresponding elastic moduli determined in the investigation of the effect of RVE size on the mechanical properties of CNT-PE composite. All RVEs are reinforced by 2.0 vol.% of well-dispersed CNTs with AR = 200. ................................................................................................................94
Table 5-8 The stiffness constants and the elastic moduli determined in the investigation of the effect of CNT volume fraction on the mechanical properties of CNT-PE composite. All RVEs of the nanocomposite were reinforced by well-dispersed CNTs with AR = 100. ................................................................................................................96
Table 5-9 The stiffness constants and the corresponding elastic moduli determined in the investigation of the effect of CNT bundle size on the mechanical properties of CNT-PE composite. All RVEs were reinforced by 3.0 vol.% of well-dispersed CNTs with AR = 200.

Table 5-10 The stiffness constants and the corresponding elastic moduli determined in the investigation of the effect of CNT morphology on the mechanical properties of CNT-PE composite.

Table 6-1 Orientation of grains in polycrystalline CNTs.

Table 6-2 Comparisons of mechanical properties and potential energy (PE) of different polycrystalline CNTs.

Table 6-3 The mechanical properties and PE of pristine/defective CNTs and graphene sheets.

Table 7-1 Parameters used in the RVEs.

Table 7-2 LJ potential parameters used in the ABC study.

Table 7-3 LJ potential parameters used in the present study.

Table 8-1 Parameters used in the RVEs with wavy (5,5) SWCNTs of length 270 Å at ~1.2 vol%.

Table 8-2 Parameters used in the RVEs reinforced with agglomerated (5,5) SWCNTs.

Table 8-3 Pull-out energies and shear stresses in the 3-tube rope/epoxy resin composites.

Table 8-4 Parameters used in calculating the ISS and the main output results of the MD study of effect of bundle size.

Table 9-1 Data of all finite element models used in investigating the electromechanical coupling of CNT-reinforced composites. All RVEs have an aspect ratio of 1 and all CNTs are (5,5) SWCNT with aspect ratio 100.

Table 9-2 Elastic moduli of the epoxy material.

Table 9-3 Strain gauge factors (piezoresistivity coefficient) for case #1 (epoxy polymer reinforced with 0.1 vol.% of SWCNTs) for different loading conditions obtained using the developed electromechanical model.

Table 9-4 Strain gauge factors predicted for RVEs with different volume fractions under uniaxial tensile and compression loading conditions.
LIST OF FIGURES

Figure 1.1 (a) Composite usage in the Boeing 787 (Credit [15]). Aerospace applications of multifunction CNT-reinforced polymer composites: (b) condition health monitoring of structure integrity (Credit [16]), (c) electrostatic dissipation during lightning strike protection (Credit [17]), and (d) electromagnetic interference shielding (Credit [18]).

Figure 1.2 (a) Schematic representations of a percolating CNT network, (b) variation of electrical conductivity (σ) with CNT concentration, and (c) break down of CNTs networks due to crack propagation.

Figure 1.3 The Proposed research program.

Figure 1.4 Modeling steps involved in the developed multiscale model.

Figure 1.5 A schematic representation of the sequence used to construct polycrystalline CNTs.

Figure 1.6 Multiscale sequence in the proposed coupled electromechanical model.

Figure 2.1 SEM images of an AFM force sensor (a) before and (b) after the pull-out of a MWCNT from a PEEK polymer (After [10]), and (c) a schematic diagram of a microdroplet test set-up (After [11]).

Figure 2.2 (a) Snapshots of a SWCNT–PE composite at the beginning, the middle, and the end of the pull-out MD simulation (After [14]), and (b) upper part shows a representation of CNT–polymer interface using beam and truss elements and lower part shows a 2D schematic representation of the pull-out simulation in the ABC model (After [15]).

Figure 2.3 (a) SEM image of aligned as-grown MWCNTs (After [24]), (b) SEM image of a poly(vinyl alcohol) reinforced with 50 wt.% of CNTs having a wide range of curvatures (After [25]), and (c) optical micrograph of an epoxy polymer containing 0.05 wt% of agglomerated MWCNTs (After [26]).

Figure 2.4 (a) An analytical model of the pull-out of a curved CNT from a polymer matrix (After [27]), and (b) snapshots of pull-out MD simulation of a CNT bundle from aligned PE polymer chains (After [23]).

Figure 2.5 Toughening mechanisms in CNT-reinforced composites: (a) TEM micrograph of a MWCNT pulled out from the matrix at a crack surface, and (b) SEM image of a crack surface bridged by double wall carbon nanotubes (After [35]).

Figure 2.6 Scaling steps involved in multiscale modeling of CNT-reinforced composites (After [15]).

Figure 2.7 (a) STM images of carbon nanotubes intramolecular junctions at three different sample (After [54]), (b) Schematic representation of the fusion of two CNT tips under high electric field condition, and (c) TEM image of a typical nanojunction (After [55]).

Figure 2.8 (a) Sequence of vacancy reconstruction into Stone Wales defects in a (16,0) armchair SWCNT (After [56]), and (b) construction of an ‘‘X’’ junction from two SWNTs of 2.0 and 0.9 nm diameters using electron irradiation where heptagonal rings are formed at the junction boundaries (After [57]).
Figure 2.9 (a) and (b) atomic and band structures of a CNT with a parallel GB, respectively, (c) and (d) atomic and band structures of a CNT with a perpendicular GB, respectively (After [62]).

Figure 2.10 (a) An atomistic model of a RVE reinforced with randomly dispersed SWCNTs, (b) an equivalent representation of the CNTs as 3D sticks, and (c) the percolating CNTs network (the blue arrows representing the direction of the electric current).

Figure 2.11 (a) The electrical conductivity of a CNT-polymer composite as a function of the CNT volume fraction (After [70]), and (b) a schematic representation of three connected CNTs and an equivalent electric circuit formed from intrinsic and tunneling resistances.

Figure 2.12 (a) The change in the electrical resistance under cyclic loading, (b) SEM image showing the formation of a microscale crack in a 90° ply, and (c) SEM image of the protruding CNTs from the matrix at the crack surface (After [98]).

Figure 2.13 (a) A percolating CNTs network in the fiber composite, (b) a schematic diagram of the equivalent resistor network, and (c) variation of the tensile load and the electric resistance with the applied tensile strain (After [98]).

Figure 2.14 (a) Transformation of the percolating networks inside the composite into equivalent parallel pathways, and (b) a schematic representation of the break down of conductive pathways in the single-edge cracked specimen (After [85]).

Figure 2.15 A schematic illustration of randomly oriented CNTs in a polymer matrix where the locations of the CNTs ends are updated under the applied strain (After [100]).

Figure 3.1 Modeling steps involved in the developed multiscale model.

Figure 3.2 Molecular structures of (a) epoxy resin (DGEBA) and (b) curing agent.

Figure 3.3 Steps used in the preparation of the polymer matrix (a) cross-linked structure, (b) distorted structure in the 3D unit cell, (c) five 80:40 cross-linked structure randomly placed in a simulation box of size 150 Å × 150 Å × 150 Å, and (d) the equilibrated system in a simulation box of size 61 Å × 61 Å × 61 Å after 25 volume reduction steps.

Figure 3.4 The simulation box used to study the interface layer: (a) before volume reduction, and (b) after equilibration.

Figure 3.5 RDF of the epoxy atoms around the embedded CNT.

Figure 3.6 MD unit cells containing a: (a) single CNT, (b) bundle of three CNTs and (c) bundle of seven CNTs.

Figure 3.7 Geometrical configurations of the bundle of CNTs: (a) bundle of three CNTs and (b) bundle of seven CNTs.

Figure 3.8 Snapshots of the transverse cross-sections of the MD unit cells containing a: (a) single CNT, (b) bundle of three CNTs and (c) bundle of seven CNTs.
Figure 3.9 Relationship between the local coordinates (1, 2, 3) of the RVE and the global coordinates (1'', 2'', 3'') of the bulk composite.

Figure 3.10 Comparison of Young’s (E) and shear (G) moduli of the nanocomposite containing randomly oriented CNTs predicted by the present multiscale model with those of ABC model [25].

Figure 3.11 Variation of the effective axial Young’s modulus (E33) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

Figure 3.12 Variation of the effective transverse Young’s modulus (E11) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

Figure 3.13 Variation of the effective axial shear modulus (G23) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

Figure 3.14 Variation of the effective transverse shear modulus (G12) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

Figure 3.15 Variation of the effective bulk modulus (K12) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

Figure 3.16 Variation of the effective Young’s modulus (E) of the nanocomposite containing randomly oriented CNTs with the CNT volume fraction.

Figure 3.17 Variation of the effective shear modulus (E) of the nanocomposite containing randomly oriented CNTs with the CNT volume fraction.

Figure 4.1 Experimental results showing wavy nature of CNTs: (a) SEM image of CNT-epoxy composites with different scales and (b) A schematic representation of agglomerated and wavy CNTS (After [19]).

Figure 4.2 Details of the multiscale model.

Figure 4.3 (a) TEM-images of a CNT-epoxy composite (After [31]), (b) A schematic representation of a wavy CNT showing the main parameters that control curvature.

Figure 4.4 MD unit cells used in the MD simulations to represent RVEs reinforced with (a) straight CNT (α=0) and (b) wavy CNT (α=0.77).

Figure 4.5 CNT bundle consists of seven CNTs used in the MD simulations to represent agglomerated nanotubes.

Figure 4.6 CNT bundle consists of three CNTs used in the MD simulations to represent agglomerated nanotubes.

Figure 4.7 Schematic representations of the applied loading conditions and the predicted elastic constants for the different loading cases.

Figure 4.8 Effect of CNT waviness on the bulk elastic moduli of CNT/epoxy composites (all nanotubes are well dispersed).
Figure 4.9 Variation of Young’s modulus and shear modulus with CNT curvature at 2.0 vol % of CNTs. ............74

Figure 4.10 Effect of CNT agglomeration on the bulk elastic moduli of CNT/epoxy composites (all nanotubes are wavy with curvature parameter α=0.54). ..........................................................75

Figure 4.11 The variation of Young’s modulus and shear modulus with the number of nanotube on the CNT bundle. ........................................................................................................76

Figure 4.12 Effect of CNT orientation on bulk elastic moduli of CNT/epoxy composites (all nanotubes are wavy with shape parameter α=0.54). ..........................................................77

Figure 5.1 Steps involved in the multiscale model: (a) an image of a CNT-reinforced composite sample, (b) an AFM image of the nanocomposite, (c) a RVE mimicking the composite microstructure with varied shapes and bundles of CNTs used as reinforcements.................................................................85

Figure 5.2 (a) Morphology and distribution state of as-received CNTs from a microstructure image measured with SEM, schematic representations of (b) two bundles of three and seven CNTs, and (c) a wavy CNT in the shape of a sine wave........................................................................................................87

Figure 5.3 RVEs with (a) SRRVE = 0.83 and reinforced with 3 CNTs, and (b) SRRVE =1.51 and reinforced with 18 CNTs. All PE chains are omitted from this figure for graphical purposes and all CNTs are SWCNTs with chirality (5,5) and AR=200. The CNT volume fraction in all RVEs is 2.0%.........................................................................................88

Figure 5.4 RVEs reinforced with (a) 1.0 vol.% (b) 3.0 vol.%, and (c) 5.0 vol.% of CNTs. All PE chains are omitted from this figure for graphical purposes and all CNTs are SWCNTs with chirality (5,5) and aspect ratio of 100.....89

Figure 5.5 RVEs reinforced with (a) 26 well dispersed CNTs, (b) 5 bundles with each consisting of three CNTs, and (c) 2 bundles with each consisting of seven CNTs. The PE chains are omitted from this figure for graphical purposes. .................................................................................................90

Figure 5.6 RVEs reinforced with (a) 26 well dispersed CNTs of different length, waviness ratios and bundle sizes, (b) 26 well dispersed CNTs, and (c) 4 bundles of CNTs. The PE chains are omitted from this figure for graphical purposes. .........................................................................................................92

Figure 5.7 Effect of RVE size: (a) the stress-strain curves obtained from uniaxial compression loading of RVEs with different sizes, and (b) the variation of Young’s modulus and number of atoms with the increase of the system size (the y-axis is normalized by the Young’s modulus of the largest RVE). .................................................................................................95

Figure 5.8 (a) The stress-strain curves obtained from uniaxial compression loading of RVEs reinforced with different CNT volume fractions, and (b) comparison between the obtained elastic properties from our MD simulations and those obtained experimentally by Gorrasi et al. [42]. (the y-axis is normalized by the Young’s modulus of neat polyethylene)..........................................................................................................97

Figure 5.9 (a) The stress-strain curves obtained from uniaxial compression loading of RVEs with different bundle sizes, and (b) the variation of Young’s modulus with the increase of the CNTs in the bundle. .............................................99
Figure 5.10 Stress-strain curves for different RVEs considered in the CNT morphology investigation obtained under uniaxial compression loading in the x-direction: (a) the normal stress along the loading direction, and (b) the normal stress perpendicular to the loading direction.

Figure 6.1 Randomly distributed grains with different sizes and shapes created using Voronoi tessellation technique: (a) 50 grains, (b) 250 grains, and (c) 500 grains.

Figure 6.2 (a) A plot of a 600 Å × 600 Å square region filled with randomly distributed grains with different sizes and shapes created using Voronoi tessellation technique. The square at the center shows the part of the system filled with randomly oriented graphene domains to create the tessellated graphene sheet. (b) Snapshot of an unequilibrated polycrystalline graphene sheet of a size 300 Å × 300 Å. The square at the bottom edge shows the part of the graphene system that is rolled to form a polycrystalline CNT. (c) An enlarged view of the graphene sheet with 4 grains. Angles of the corresponding crystallographic direction of the grains are determined with respect to the horizontal axis (see Table 6.1 for details). (d) and (e) procedures used to create the polycrystalline CNT.

Figure 6.3 Atomic structure of a tilt GB in graphene separating two crystalline domains misoriented by \( \varphi = \theta_L + \theta_R = 280 + 70 = 350\). \(a_1\) and \(a_2\) are the unit vectors of graphene lattice.

Figure 6.4 Different cases of polycrystalline CNTs: (a) CNT with random GBs. (b) CNT with helical GBs. (c) Parallel GB to the CNT axis. (d) Transverse GB to the CNT axis.

Figure 6.5 Atomic structures of CNTs with a horizontal GB and different diameters.

Figure 6.6 Stress-strain curves of the pristine CNT and polycrystalline CNTs with random GBs (corresponding to first 4 rows of Table 6.1).

Figure 6.7 The variation of the PE of CNTs with random GBs (corresponding to rows 2 to 4 of Table 6.1).

Figure 6.8 Averaged stress-strain curves of pristine and polycrystalline CNTs.

Figure 6.9 Simulation of failure of a CNT with random GBs under tensile loading. (a) Unstrained CNT, (b) CNT strained under tension at an average strain rate of \(1.25 \times 10^9\) s\(^{-1}\). (c) Fracture nucleates at GB and the interiors of the grains remain stress free. (d) A global fracture of a CNT.

Figure 6.10 Atomic structures of three CNTs with different diameters.

Figure 6.11 Variation of (a) the potential energy and (b) the uniaxial stress with the applied uniaxial strain of CNT with circumferential GB at different temperatures.

Figure 6.12 The variation of (a) the fracture strength and (b) the fracture strain with temperature of CNT with circumferential GB of diameter 9 Å.

Figure 7.1 RDF of the epoxy atoms around the embedded CNT (transverse cross-sectional view of the equilibrated RVE is shown in the inset).

Figure 7.2 MD unit cell containing a single CNT embedded in the epoxy matrix.
Figure 7.3 Schematics of CNT-reinforced epoxy composite at various displacements during CNT pull-out process .............................................................................................................................................. 131
Figure 7.4 Schematic of the RVE [35] ......................................................................................................................................................................................................................... 132
Figure 7.5 Polymer representation and pull-out boundary conditions [45] ............................................................................................................................................................................. 134
Figure 7.6 Effect of embedded CNT length on the ISS ........................................................................................................................................................................................................ 135
Figure 7.7 Effect of CNT-polymer interface thickness on the ISS .................................................................................................................................................................................. 136
Figure 7.8 Effect of LJ cut-off distance on the ISS ............................................................................................................................................................................................................ 137
Figure 7.9 Effect of CNT diameter on the ISS .............................................................................................................................................................................................................. 138
Figure 8.1. Schematic diagram showing the pull-out of partially embedded CNT from Epoxy matrix and the applied boundary conditions ................................................................................................................................. 145
Figure 8.2 Curved nanotubes in (a) an SEM micrograph of as-received CNTs and (b) an AFM micrograph of a CNT/epoxy composite ................................................................................................................................................................................................. 146
Figure 8.3 Details of assumed wavy carbon nanotube: (a) the parameters governing the sinusoidal form of the CNTs, and (b) the four CNTs used in the simulations of wavy CNTs .................................................................................................................................................................................. 147
Figure 8.4 MD unit cells used in the MD simulations to represent RVEs reinforced with (a) straight CNT (α=0), and (b) wavy CNT (α=0.23). ........................................................................................................................................................................................................................................ 147
Figure 8.5 Agglomerated nanotubes in STEM micrographs of (a) as-received CNTs and (b) a CNT/PVP composite (After [43]). .................................................................................................................................................................................................................................................. 148
Figure 8.6 Molecular models of epoxy matrix reinforced with: (a) single CNT, (b) bundle of three CNTs, (c) bundle of seven CNTs, (d) bundle of nineteen CNTs, and (e) bundle of thirty-seven CNTs .......................................................................................................................................................................................................................................................... 149
Figure 8.7 Snapshots of the CNT/epoxy composite during the pull-out of a wavy CNT (α=0.14) ........................................................................................................................................................................................................................................ 153
Figure 8.8 Binding energy plots during the pull-out of CNTs with different curvatures from epoxy matrix as a function of pull-out displacement .................................................................................................................................................................................................................................................................................................................. 154
Figure 8.9 Variation of pull-out force throughout the pull-out process of CNTs with different curvatures from epoxy matrix as a function of pull-out displacement .................................................................................................................................................................................................................................................................................................................. 155
Figure 8.10 Snapshots of the nanocomposite system at the middle of the pull-out of: (a) a single CNT, (b) a bundle of three CNTs, (c) a bundle of seven CNTs, (d) a bundle of nineteen CNT and (e) a bundle of thirty-seven CNT. .................................................................................................................................................................................................................................................................................................................. 156
Figure 8.11 Binding energy plots during the pull-out of CNT bundles of different sizes and a well-dispersed individual CNT from epoxy matrix as a function of pull-out displacement .................................................................................................................................................................................................................................................................................................................................................. 157
Figure 8.12 Variation of the ISS as a function of the number of CNTs inside the bundle .................................................................................................................................................................................................................................................................................................................................................................................. 159
Figure 8.13 Variation of the interfacial shear stress with the number of CNT layers and waviness ratio of the CNTs inside the pulled-out bundles.......................

Figure 9.1 Coupling sequence in the proposed electromechanical model: (a) MD model of the composite constituents, (b) hybrid FE-MD model, and (c) percolating CNTs network identified using the developed electrical model. ....

Figure 9.2 Schematic representations of Monte Carlo method: (a) randomly distributed CNT showing the parameters governing its location and orientation, (b) RVE prior to applying periodic boundary conditions and (c) RVE after applying the periodic boundary.

Figure 9.3 The algorithm used to identify the percolating networks in the developed electrical model. The input parameters to this simulation step are CNT length, diameter, RVE size, and number of samples.

Figure 9.4 Sequence adopted in building the equivalent electrical circuit: (a) dispersing the required number of CNTs inside the RVE, (b) transforming all CNTs into 3D line segments, (c) backbone of the percolating network that enables the current to be transmitted, and (e) equivalent electric circuit of the percolating network.

Figure 9.5 Finite element models representing cubic RVEs, with side length of 68 nm reinforced with (a) 0.1 vol. %, (b) 0.2 vol. %, and 0.3 vol. % of CNTs. All models are meshed with quadratic tetrahedral elements.

Figure 9.6 The influence of RVE size on (a) the electrical and (b) percolation properties of CNT-reinforced composites obtained with Monte Carlo simulations and modified nodal analysis technique.

Figure 9.7 Comparison of predicted electrical conductivity with existing experimental data [49,50].

Figure 9.8 Snapshots of the FE model for case # 1 (Vol 0.1%) (a) before and (b) after applying a uniaxial tensile strain of 10% along x-direction. CNTs percolating network along x-direction identified using the developed electrical model for (c) initial and (d) deformed RVE.

Figure 9.9 The finite element model used to determine the structural response. (b) A close view of one of the contacts between adjacent CNTs before (closed percolating path) and after (open path) applying an external load.

Figure 9.10 The variation of (a) the electrical conductivity and (b) the change in electrical resistance over the initial resistance ($\Delta R/R_0$) of the RVE for case #1 (0.1 vol. %) with the applied strain for different loading conditions.

Figure 9.11 CNTs percolating networks along x-direction identified using the developed electrical model for RVEs reinforced with (a) 0.1%, (b) 0.2% and (d) 0.3% volume fractions of CNTs.

Figure A3.1 SEM image of as-received MWCNTs.

Figure A3.2 CNTs distribution in the polymer matrix: (a) AFM and (b) SEM images of an epoxy polymer reinforced with uniformly distributed 1.0 wt.% of CNTs.

Figure A3.3 SEM images of an epoxy polymer reinforced with 4.0 wt.% of CNT.
LIST OF APPENDICES

Appendix 1: Basics of MD simulations ............................................................................................................194

Appendix 2: Eshelby Tensor in Micromechanical Model ..................................................................................200

Appendix 3: Experimental Investigations .....................................................................................................201
# ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two-Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-Dimensional</td>
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<tr>
<td>ABC</td>
<td>Atomistic-based continuum</td>
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<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
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<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>DWCNT</td>
<td>Double-walled carbon nanotube</td>
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<tr>
<td>FEM</td>
<td>Finite element method</td>
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<tr>
<td>FRPs</td>
<td>Fibre reinforced polymers</td>
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<tr>
<td>GB</td>
<td>Grain boundary</td>
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<tr>
<td>ISS</td>
<td>Interfacial shear strength</td>
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<tr>
<td>Lj</td>
<td>Lennard-Jones potential</td>
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<tr>
<td>MD</td>
<td>Molecular dynamics</td>
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<tr>
<td>MM</td>
<td>Micromechanics</td>
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<tr>
<td>MNA</td>
<td>Modified nodal analysis</td>
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<tr>
<td>MWCNT</td>
<td>Multi-wall carbon nanotubes</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
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<tr>
<td>QM</td>
<td>Quantum mechanics</td>
</tr>
<tr>
<td>RVE</td>
<td>Representative volume element</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SHM</td>
<td>Structural health monitoring</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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SWCNT  Single-wall nanotube
TEM  Transmission electron microscopy
TETA  Triethylene tetramine
vdW  van der Waals

SYMBOLS

Å  Angstrom
\(d_{\text{CNT}}\)  Diameter of a CNT
\(d_{\text{cutoff}}\)  Cut-off distance
\(d_{\text{tunnel}}\)  Tunneling characteristic length
\(e\)  Electron charge
\(h\)  Planck’s constant
\(h_{\text{vdW}}\)  van der Waals separation distance
\(L_{\text{CNT}}\)  Length of a CNT
\(L_{\text{RVE}}\)  Side length of the RVE
\(M\)  Total number of conduction channels in a CNT
\(fs\)  Femtosecond
\(Hr\)  Hour
\(min\)  Minute
\(nm\)  Nanometer
\(ns\)  Nanosecond
\(R\)  Electrical resistance
\(R_{\text{contact}}\)  Contact/Tunneling resistance
\(S^RVE\)  Eshelby tensor
\(Rand\)  Uniformly distributed random number in the interval (0,1)
\(L_{\text{CNT}}\)  Length of CNT
\(vol\)  Volume fraction
\(\sigma_{\text{CNT}}\)  Intrinsic electrical conductivity of the CNT
\(\phi\)  Azimuthal angle
\(\theta\)  Polar angle
Chapter 1.
Introduction and Justification

Summary: In this chapter, we describe the details of the research to be undertaken, justify the reasons for conducting this research, outline the research objectives, and present the method of approach adopted to treat these objectives. Additionally, a summary of the layout of the thesis is provided.

1.1 Introduction

Owing to their remarkable mechanical and physical properties, CNTs have emerged as one of the most promising reinforcement materials to tailor the properties of polymer-based nanocomposites [1]. Typically, the diameters of single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) are in the range of 0.8 to 2 nm and 5 to 20 nm, respectively [2]. Their aspect ratio, longitudinal Young’s modulus, and tensile strength can reach up to 1000s [3], 1 TPa [4], and 100 GPa [5], respectively. Furthermore, in view of their one-dimensional nature, the electrons in the CNTs move ballistically without scattering [6]. They can carry current densities of up to 109 A/cm² [7]. In view of these exceptional properties, a few weight percentage of CNTs can significantly improve the mechanical, electrical, and thermal properties of multifunctional nanocomposite materials [8]. Such composites have found their way into different industrial applications such as electrostatic-assisted painting, load-bearing applications in sporting goods industry, and enhanced fiber composites in wind turbine blades and patrol boats [2,8]. Furthermore, with the increasing use of composite materials in the aerospace industry, more advanced applications for CNT-reinforced composites that require multifunctional properties are being explored including strain sensing, electromagnetic (EM) interference shielding of electronics, and lightning strike protection for aerospace vehicles [2,8]; see Fig. 1.1.

The improvement in mechanical and fracture properties of CNT-reinforced composites is attributed to the reinforcement effect and the crack bridging mechanism of the embedded CNTs that require high pull-out energy of the nanotubes [9]. Additionally, dispersing a small fraction of CNTs into an insulating polymer transforms it into an electrically conductive material due to the formation of percolating CNT networks that work as conductive pathways for the electric current
[10,11]; as depicted in Fig. 1.2(a). The electrical conductivity increases with the increase in the CNT concentration and this change in conductivity can be determined with the aid of an appropriate percolation theory [8], as shown in Figure 1.2(b). In general, electric current is transmitted through the nanocomposite in two forms: (i) ballistic transport of electrons along CNTs, and (ii) electron tunneling between sufficiently close CNTs [12–14]. Furthermore, the electrical resistance of a CNT-polymer composite change in response to external loads (see Fig. 1.2(c)), indicating a highly sensitive electromechanical coupling behavior that makes them a potential candidate for structural health monitoring (SHM) applications, where the piezoresistive composite can be used for mapping strain, detecting damage, and monitoring crack initiation and propagation (see Fig. 1.2(c)) [9-14].

![Composite usage in the Boeing 787](image)

**Figure 1.1** (a) Composite usage in the Boeing 787 (Credit [15]). Aerospace applications of multifunction CNT-reinforced polymer composites: (b) condition health monitoring of structure integrity (Credit [16]), (c) electrostatic dissipation during lightning strike protection (Credit [17]), and (d) electromagnetic interference shielding (Credit [18]).
With the growing use of CNT-polymer composites commercially, designers are faced with several challenges relating to the feasibility, applicability and reliability of these novel composites. Furthermore, due to the enormous computational cost required for atomistic modeling of large scale systems representing realistic nanocomposites structures and the inherent technical difficulties in preparing and testing their multifunctional properties at the nanoscale level, several analytical and numerical techniques were developed to model these advanced materials [19,20]. At the nanoscale, the atomic structures of the CNT and the surrounding polymer matrix cannot be considered as a continuum medium, and the bulk elastic properties can no longer be obtained using traditional continuum mechanics approaches. As a result, multiscale modeling schemes have been proposed to bridge the atomic structure of the nanocomposite and the bulk behavior of the material [21–23]. In general, multiscale modeling of nanocomposites is achieved in two consecutive steps. At the nanoscale level, for example, both molecular dynamics (MD) simulations and atomistic based continuum (ABC) technique can be used to determine the effective elastic properties of a representative volume element (RVE) consisting of a CNT embedded in a polymer matrix [24]. At the bulk level, either micromechanical approaches or finite element (FE) simulations can be used to scale up the nanoscale properties to determine the effective properties of the composite at the microscale [24]. These multiscale techniques were used to investigate the reinforcement mechanisms of CNTs and their influence on the overall performance of the nanocomposite [21–24]. To the best of the authors' knowledge, no MD simulations have been carried out to examine the influence of CNT agglomeration and morphology on the reinforcement and toughening mechanisms of the nanocomposite.

\[\text{Figure 1.2} \quad (a) \text{ Schematic representations of a percolating CNT network, (b) variation of electrical conductivity (}\sigma\text{) with CNT concentration, and (c) break down of CNTs networks due to crack propagation.}\]
1.2 Justification for the study

Despite the remarkable extraordinary properties of CNTs, the reported enhancements in the mechanical properties of their polymer composites [25,26] are significantly lower than what analytical and numerical studies have predicted [21–24]. There are two main reasons for this discrepancy: the first is due to the inability of current modeling techniques to represent the actual behavior of nanocomposites [21] and the second is concerned with the difficulties associated with atomistic tests as well as the large discrepancy and inconsistencies that exist among these tests. For example, poor dispersion, agglomeration, and aggregation of CNTs lead to inferior properties because of the limited stress transfer from the matrix to the reinforcing CNTs [27]. Additionally, because of the extremely high aspect ratio and very low bending stiffness of the CNTs, they tend to bend or unfold when dispersed in polymer matrices [28]. Due to the induced curvature, the elastic moduli of the nanotubes and consequently the nanocomposite varies significantly in all directions [29]. Other parameters that influence the resulting properties of nanocomposite include the quality of CNTs used, their purities, geometry and aspect ratios as well as their orientation within the nanocomposite [1].

Similarly, current analytical models of nanocomposite materials contain several assumptions that undermine the accuracy of their findings. Firstly, they neglect the discrete nature of CNTs by considering them as solid cylinders. Secondly, they assume perfect bonding between the embedded CNTs and the surrounding polymer matrix unlike actual nanocomposites where the adhesion between its constituents is mostly caused by weak nonbonded interactions such as van der Waals forces [24]. Thirdly, they assume CNTs to be linearly elastic and isotropic. Finally, they neglect the interactions between the dispersed CNTs due to the dilute concentration assumption. Moreover, most existing multiscale models unrealistically assume that CNTs are straight, defect free, well-dispersed, and uniformly distributed reinforcements [24]. These assumptions result in overestimated predictions of the mechanical performance of the composite and limit our ability to utilize them in engineering applications. The use of MD offers an appropriate and an effective means to deal with these kinds of problems without having all these unnecessary assumptions [30], but at a computational cost. To the best of the authors' knowledge, no MD simulations have been carried out to examine the influence of CNT agglomeration and morphology on the reinforcement and toughening mechanisms of the nanocomposite.
CNT-based sensors have often been considered unsuitable for practical applications due to their complex unpredictable nature of their behavior [31]. To overcome this problem, polymer adhesives were introduced to prevent the breakdown of conductive pathways inside the nanocomposite that are formed from the percolating CNT-networks [32]. The electromechanical behavior of CNT-polymer composites is controlled by the change in the tunneling and intrinsic resistance of the percolating CNTs under the applied strain. In order to successfully utilize such nanocomposites in structural health monitoring applications, a few rudimentary analytical and numerical modeling techniques were developed over the past decade to study their piezoresistive behavior [9-14]. However, the attempts to investigate CNT-reinforced composites came short of capturing the complexity of the material structure at the nanoscale level due to their inability of coupling the electrical and mechanical properties at different length scales. As a result, the electromechanical coupling mechanisms of CNT-polymer composites remain unclear. For example, the break down and formation of percolating CNT networks due to the complex morphology of CNTs (i.e., geometry, orientation, agglomeration, processing), and the induced disruption in the percolating CNT network caused by the initiation and evolution of damage [33], cannot be modeled by simple reorientations models such as the one described in [34]. Furthermore, conductive CNT-reinforced composites that use special stretchable polymers can experience strains up to 400%, and hence require a more advanced electromechanical modeling approach [32].

Finally, due to the inherent limitations of fabrication and purification processes, CNTs typically contain a variety of crystallographic orientations and defects [35]. Furthermore, under certain circumstances, grain boundaries (GBs) are deliberately introduced by fusing two CNT segments together for the purpose of tailoring their electronic properties to suit the requirements of a particular application [36]. The effects of relatively simple defects such as atom vacancies, doping, Stone-Wales, and hybridization, on the thermomechanical properties of CNTs have been studied in the literature; see, e.g., Refs. [37,38]. However, the mechanical properties of CNTs with GBs have not yet been fully explored and investigated. As a result, we lack comprehensive understanding of the influence of these GBs, which may limit the exploitation of the properties of polycrystalline CNTs.
From the conducted literature review, it can be concluded that a reliable multiscale model that considers CNT morphology, dispersion state, and orientations at the nanoscale is highly desirable as it will overcome the inherent and artificially imposed limitations in current modeling techniques. Additionally, a fully coupled electromechanical model will successfully overcome the shortcomings of current modeling approaches. The present study is intended to fill this gap in the literature.

1.3 Objectives

It is therefore the objective of this research program to:

(i) Conduct comprehensive MD simulations of the pull-out process of CNTs of different curvatures and bundle sizes from polymer matrix to determine the effect of morphology and dispersion state on the interfacial shear strength and toughening mechanism of CNT-reinforced thermoset composites making use of SEM and AFM tests.

(ii) Develop a novel multiscale model based on MD simulations and the Mori-Tanaka micromechanical method to determine the enforcement mechanism of the CNTs at the nanoscale and the effective mechanical properties of nanocomposites with realistic morphologies at the bulk level. Additionally, determine the effects of GB orientation, grain size and crystallographic direction, nanotube curvature, and temperature on the mechanical and fracture properties of polycrystalline CNTs using MD simulations.

(iii) Conduct large-scale atomistic simulations of RVEs of actual nanocomposite systems reinforced by CNTs with aspect ratio in the range of 100s to overcome the inherent limitations in micromechanical techniques and accurately capture the elastic behavior of the nanocomposite.

(iv) Conduct Monte Carlo simulations to determine the electric and percolation properties of CNT reinforced composites using a search algorithm for percolating CNT networks followed by modified nodal analysis to calculate their effective resistances. Additionally, develop a coupled electromechanical model that uses the output from an FE model of a large-scale RVE under different loads to update the locations of CNTs inside the electrical model and determine the corresponding electrical response of the nanocomposite.
1.4 Method of Approach

Figure 1.3 divides the research program into six main components: (1) investigating the interfacial properties of CNT-reinforced composites via MD pull-out simulations, (2) developing a novel multiscale model based on MD simulations and the Mori-Tanaka micromechanical technique for pristine and defective CNTs, and their polymer nanocomposites, (3) conducting large scale MD simulations of nanocomposites with realistic microstructures, (4) developing a coupled electromechanical model based on hybrid finite element model and the modified nodal analysis method, and (5) measuring the morphology and dispersion state of a typical CNT-epoxy composite using SEM and AFM.

![Research Program Diagram]

**Figure 1.3** The Proposed research program.

A novel multiscale model is developed to determine the effect of dispersion state, morphology, and alignment of CNTs on interfacial and mechanical properties of CNT-reinforced polymer composites. The coupling between nano- and micro-levels properties was achieved in two consecutive steps, as shown in Fig. 1.4. Firstly, RVEs reinforced with well-dispersed and agglomerated CNTs of different curvatures ranging from straight to severely curved were...
modeled to determine their nanoscale properties using atomistic simulations. The interfacial shear strength between the embedded CNTs and the surrounding matrix is obtained via MD pull-out simulations. Furthermore, the stiffness constants of the RVEs are determined using the constant-strain energy minimization method. The properties of the nanocomposite constituents, obtained from the MD simulations, are then scaled up to the bulk level using the Mori-Tanaka micromechanical technique.

Additionally, large-scale -up to one million atoms- RVEs reinforced with randomly dispersed CNTs are constructed and modeled with MD simulations to directly determine the microscale response of nanocomposites with realistic microstructures. This direct modeling approach can predict the material properties more accurately than multiscale approaches due to their inherent limitations and oversimplification of the atomic nature of the CNTs and the surrounding interphase polymer layer.

Furthermore, the mechanical and fracture properties of polycrystalline CNTs of different diameters at both room and elevated temperatures were determined using MD simulations. A program based on the Voronoi tessellation method and Delaunay triangulation is developed to generate the atomistic descriptions of polycrystalline graphene. The constructed graphene sheets are then rolled into tubular shapes to construct CNTs with a variety of GB morphologies, as shown in Fig. 1.5. The elastic moduli, fracture strength, and fracture strain are then determined from the strain-stress curves obtained from the tensile MD simulations.

![Figure 1.4 Modeling steps involved in the developed multiscale model.](image-url)
The proposed coupled multiscale electromechanical model is developed in three steps, as shown in Fig. 1.6. Firstly, MD simulations are used to determine the transversely isotropic stiffness tensor of a SWCNT and the isotropic stiffness tensor of pure epoxy polymer. Secondly, a Monte Carlo based algorithm is developed to randomly disperse CNTs in the polymer matrix. Large-scale three-dimensional (3D) FE simulations are performed to determine the structural response of the RVE under compression, tensile, and shear loads. The obtained elastic moduli at the nanoscale level are used to define the material properties in the FE model. Thirdly, an advanced algorithm is developed to identify the percolating CNT networks in all directions and transform them into an equivalent electrical circuit formed from tunneling and intrinsic resistances. The deformed RVE is incorporated into the electrical model by updating the coordinates of the CNTs in the percolating network and the electrical conductivity is then calculated using the modified nodal analysis method. The strain gauge factor of the composite is obtained from the relationship between the change in the electrical resistance and the applied strain.
1.5 Plan and Organization of Thesis

Following this brief introduction, Chapter 2 provides a critical review of modeling and characterization of multifunctional CNT-reinforced polymer. This paper-based thesis incorporates seven journal papers, each in a separate chapter. The conducted work is organized in three main parts. The first part (Part I) investigates the mechanical properties of CNTs, pure polymers, and CNT-reinforced polymer composites using MD simulations and micromechanics modeling technique. This part consists of four chapters:

(i) Chapter 3 presents the crosslinking mechanism of resin and curing agents of epoxy polymer, interphase layer characteristics, and effects of alignment on the elastic properties of the nanocomposite;

(ii) Chapter 4 outlines the developed multiscale modeling approach of CNT-epoxy composites with different CNT morphologies and dispersion states based on MD simulations and Mori Tanaka micromechanical technique;

(iii) Chapter 5 outlines the developed large-scale atomistic models of CNT-polyethylene composites with realistic microstructures; and

(iv) Chapter 6 outlines the modeling procedure of polycrystalline CNTs and presents the effects of GBs, curvature, and temperature on their elastic and fracture properties.

The second part (Part II) investigates the interfacial properties of CNT-epoxy composites using pull-out MD. This part consists of two chapters:

(i) Chapter 7 investigates the effects of CNT length and diameter, CNT-polymer interface thickness, and Lennard-Jones (LJ) cut-off distance on the interfacial shear strength; and

(ii) Chapter 8 investigates the effects of waviness and agglomeration of CNTs on the interfacial properties.

The third part (Part III) investigates the electrical and piezoresistive properties of CNT-reinforced composites. This part is contained in chapter 9, where the detailed of the developed novel multiscale electromechanical model are presented.
Finally, in Chapter 10, we summarize the main conclusions and identify the original contributions of the thesis, and propose recommendations for future research on modeling of multifunctional nanocomposite materials.

1.6 References

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Chapter 2. 
Literature Review

Summary: For the sake of completeness and continuity, I provide herein a literature review covering the background for the entire thesis. The reader must recognize as a result of using paper-based format in this dissertation, there may be some overlap in the literature review of the relevant chapters. This literature review on multiscale modeling of CNT-reinforced composites is divided into six sections. The first addresses modeling and characterization of the interfacial shear strength. The second discusses multiscale modeling techniques of the mechanical properties. The third summarizes previous studies on polycrystalline CNTs. The fourth addresses the electrical and percolation properties. The fourth outline modeling and characterization techniques of the electromechanical coupling behavior. The last section provides a brief review of the MD method and the parameters that govern the accuracy and reliability of its results.

2.1 Modeling and characterization of interfacial properties

The mechanical performance of CNT-reinforced composites is significantly influenced by the interfacial properties between the dispersed CNTs and the surrounding matrix [1]. The dispersed CNTs reinforce the matrix by sharing the applied load until either the failure of the interface or the fracture of the CNTs. The maximum shear stress that the interface can resist before the deboning starts is called the interfacial shear stress (ISS) [2] and its value determines the efficiency of stress transfer from the matrix to the embedded nanotubes [3]. Different parameters determine the reinforcement effect of the CNTs; including dispersion quality, alignment, existing defects, and morphology [4,5]. The impact of these parameters on the interfacial properties and the resulting mechanical properties were studied experimentally, theoretically, and numerically over the past decade [6]. For example, several experimental studies have been carried out to investigate the interfacial characteristics of CNT-reinforced composites using direct methods such as pull-out (see Fig. 2.1(a) and (b)) and microdroplet tests (see Fig. 2.1(c)) or indirect methods such as the fragmentation test or Micro-Raman spectroscopy [7–9]. The ISS between CNTs and polymers was estimated to be as high as 500 MPa, which is more than one order of magnitude higher than those obtained in conventional composites [9].
Figure 2.1 SEM images of an AFM force sensor (a) before and (b) after the pull-out of a MWCNT from a PEEK polymer (After [10]), and (c) a schematic diagram of a microdroplet test set-up (After [11]).

In spite of this relatively high interfacial strength, the enhancement of the mechanical properties was lower than expected due to the sliding of CNTs in the agglomerated bundle [7]. Cooper et al. [8] reported ISS in the range of 35 to 376 MPa. The large variation in these values was attributed to several variances in the pull-out test, including the embedded length, the bundle size, and the formation of covalent bonds between CNTs and the surrounding polymer along the interface.

Due to the technical difficulties inherent in preparing and testing of CNT-reinforced polymer composites at the nanoscale level, different analytical and numerical techniques have been developed to predict their interfacial properties. Atomistic pull-out simulations were conducted using both MD simulation (see Fig. 2.2(a)) and ABC technique to calculate the change in the pull-out force (see Fig. 2.2(b)). For example, Liao and Li [12] studied the interfacial characteristics of a CNT-reinforced polystyrene composite system using MD simulations. They reported that the CNT-matrix bonding arises from non-bonded electrostatic and van der Waals (vdW) interactions, deformation induced by these interactions, and mismatch in the coefficients of thermal expansion. Their CNT pull-out simulation results suggest that the interfacial shear stress of the CNT-polystyrene system is about 160 MPa; significantly higher than conventional carbon fiber composite systems. Furthermore, an ABC model was developed to study nanocomposite systems by integrating the atomistic constitutive laws within the continuum framework in a 3D FE model. The CNT was modeled as a space-frame-like structure where the adjacent atomic bonds were considered as a load-bearing beam element, as shown in Fig. 2.2(b). Nodes were used to connect
the beam elements to form the CNT structure, while truss elements were used to model the vdW interactions at the CNT-polymer interface [3,13].

Figure 2.2 (a) Snapshots of a SWCNT–PE composite at the beginning, the middle, and the end of the pull-out MD simulation (After [14]), and (b) upper part shows a representation of CNT–polymer interface using beam and truss elements and lower part shows a 2D schematic representation of the pull-out simulation in the ABC model (After [15]).

The full potential of CNTs as a reinforcement material is limited by the tendency of nanotubes to agglomerate and deform locally into wavy shapes [16,17] (see Fig. 2.3). Waviness and agglomeration of CNTs are inherent to the fabrication processes of CNT-reinforced composites [16]. Due to their high surface energy and surface area, CNTs tend to agglomerate and aggregate into bundles [18]. The presence of agglomerates limits the stress transfer between the nanotubes inside the bundle and from the matrix to the CNTs, leading to a nanocomposite with inferior properties [7]. Furthermore, due to their high aspect ratio and low bending stiffness, CNTs tend to bend or unfold when dispersed in polymer matrices [19]. Whilst determining their impact on the interfacial properties is essential in understanding how reinforcing mechanisms work, measuring it experimentally via direct Pull-out tests is challenging, especially when dealing with SWCNTs [10]. To overcome these difficulties, different analytical and numerical techniques have emerged to handle this problem [20,21]. For example, Chen et al. [22] developed an analytical
model to study the effect of CNT waviness on the interfacial properties of CNT reinforced composites. They characterized the pull-out process into three consecutive stages: the bonded stage, the debonding stage, and the sliding stage, as shown in Fig. 2.4(a). Their results showed that fibers with more curvature require more stress and energy to achieve a complete pull-out from the surrounding matrix. Lu et al. [23] studied the effect of CNT agglomeration of the interfacial properties by conducting pull-out MD simulations of a bundle of seven CNTs from PE matrix, as shown in Fig. 2.4(b).

**Figure 2.3** (a) SEM image of aligned as-grown MWCNTs (After [24]), (b) SEM image of a poly(vinyl alcohol) reinforced with 50 wt.% of CNTs having a wide range of curvatures (After [25]), and (c) optical micrograph of a liquid epoxy polymer containing 0.05 wt% of agglomerated MWCNTs (After [26]).

**Figure 2.4** (a) An analytical model of the pull-out of a curved CNT from a polymer matrix (After [27]), and (b) snapshots of pull-out MD simulation of a CNT bundle from aligned PE polymer chains (After [23]).
2.2 Modeling and characterization of mechanical properties

CNTs are ideal reinforcements for polymers [2] because of their outstanding mechanical properties, low density, high aspect ratio, and exceptionally high surface area to weight ratio [28]. Understanding the nanocomposite behavior and the associated reinforcement mechanism at the atomic level is very critical in utilizing this new material at industrial scale [29-31]. A number of experimental, numerical, and theoretical studies have been conducted to investigate the potential use of CNTs as reinforcing fibers [7,31-33]. An earlier attempt was made by Schadler et al. [34] to measure the mechanical properties of CNT-reinforced polymer composite. They reported that Young’s modulus in tension and compression can be improved by as much as 20% and 45%, respectively, at 5 wt% of CNTs. Allaoui et al. [32] managed to achieve a 200% increase in Young’s modulus of epoxy with only 1 wt% of nanotubes. Furthermore, the improvement in composite fracture toughness was attributed to the crack bridging mechanism of the embedded CNTs and the high energy required to pull out these nanotubes [35], as shown in Fig. 2.5(a) and 2.5(b).

However, despite the remarkable elastic properties of CNTs, the reported results in the literature show a limited enhancement in the effective elastic properties of their nanocomposites compared to those predicted theoretically and numerically. There exist numerous reasons for this discrepancy; including, poor dispersion of the CNTs, agglomeration and aggregation leading to inferior properties, poor interfacial properties resulting in limited stress transfer and load sharing [15]. Other parameters that influence the resulting properties of nanocomposites include the quality of CNTs used, their purities, geometry and aspect ratios as well as their orientations within the polymer matrix [36]. For instance, micro-Raman spectroscopy was used by Ajayan et al. [7] to measure the local elastic behavior of individual SWCNT bundles in epoxy-based nanocomposite. They noticed that the efficiency of the stress transfer and hence the enhancement of the mechanical properties was lower than what was expected due to the sliding of the CNTs in the agglomerated bundles. Meguid and Sun [33] showed that at higher CNT concentrations the mechanical properties of the nanocomposite were found to deteriorate due to the formation of CNT agglomerates, which act as stress concentrators. Furthermore, due to the induced curvature, the elastic moduli of the nanotubes and consequently the nanocomposite vary significantly in all directions [4].
Due to the enormous computational cost required for atomistic modeling of microscale RVEs of CNT-reinforced composites with realistic microstructures and the inherent technical difficulties in preparing and testing their multifunctional properties, several analytical and numerical techniques were developed to model these advanced materials [37-40]. At the nanoscale, the atomic structures of the CNT and the surrounding epoxy matrix cannot be considered as a continuum medium, and the bulk elastic properties can no longer be obtained using the traditional continuum mechanics approaches. As a result, several multiscale modeling schemes were proposed to bridge the atomic structure of the nanocomposite at the nanoscale with the material behavior at the microscale level [41-45]. In general, multiscale modeling of nanocomposites is achieved in two consecutive steps, as shown in Fig. 2.6. First, MD simulations and ABC modeling are used to obtain the effective elastic properties of a RVE consisting of a CNT embedded in a polymer matrix [15]. Second, micromechanical models and FE simulations are used to scale up the obtained properties at the nanoscale to the bulk level [46-48]. These multiscale techniques were used by several research groups to investigate the reinforcement mechanisms of CNTs in polymers and to evaluate the impact of dispersion state, alignment, morphology, and chemical functionalization of CNTs on the overall performance of the composite [2].
Figure 2.6 Scaling steps involved in multiscale modeling of CNT-reinforced composites (After [15]).

2.3 Modeling of CNTs with grain boundaries

Due to the inherent limitations of fabrication and purification processes, CNTs typically contain a variety of crystallographic orientations and defects [49]. Figure 2.7 shows STM and TEM images of CNT intramolecular junctions where two CNT segments were connected with Stone-Wales defects through vacancy reconstruction, as shown in Fig. 2.8. The common domain interface, grain boundary (GB), can be regarded as a one-dimensional array of dislocations [50]; some experimental studies also provided evidence of the existence of GBs in CNTs [51,52]. Under certain circumstances, GBs are deliberately introduced for the purpose of tailoring the electronic properties of CNTs to suit the requirements of a particular application. For example, Yao et al. [53] introduced pentagon and heptagon defects into the hexagonal carbon lattice to fuse together two nanotube segments of different atomic and electronic structures with the aim of creating intramolecular metal-metal, metal-semiconductor, or semiconductor-semiconductor junctions.
Figure 2.7 (a) STM images of carbon nanotubes intramolecular junctions at three different sample (After [54]). (b) Schematic representation of the fusion of two CNT tips under high electric field condition, and (c) TEM image of a typical nanojunction (After [55]).

Figure 2.8 (a) Sequence of vacancy reconstruction into Stone Wales defects in a (16,0) armchair SWCNT (After [56]), and (b) construction of an “X” junction from two SWNTs of 2.0 and 0.9 nm diameters using electron irradiation where heptagonal rings are formed at the junction boundaries (After [57]).

In another study by Yao et al. [58], a well-controlled temperature-mediated growth of intramolecular junctions in CNTs was achieved by changing the temperature during the process. That particular study outlined a potential approach for growing intramolecular junctions in CNTs of different sizes and orientations at desired locations. This is important for tailoring CNT-based electronic circuits. The effects of relatively simple defects such as atom vacancies, doping, Stone Wales, and hybridization on the mechanical properties of CNTs were studied extensively in the literature [59-61]. On the other hand, only electrical properties were studied for CNTs with engineered defects such as grain boundaries. For instance, the electronic properties of polycrystalline CNTs were investigated by Wang et al. [62] using density-functional theory by considering both parallel and perpendicular GBs to the tube axis, as shown in Fig. 2.9. That study...
reported that the CNTs with parallel GBs have a narrow or zero band gap (<0.16 eV) which is independent of the misorientation angle and the diameter of the CNT (see Fig. 2.9 (b)). On the other hand, CNTs with perpendicular GBs show a slightly large band gap (up to 0.6 eV), as shown in Fig. 2.9 (d). More recently, Lehmann et al. [50] demonstrated that GBs are a viable tool to tailor the thermal properties of carbon-based nanomaterials, paving the way for the design of new thermoelectric nanodevices.

![Figure 2.9](image)

Figure 2.9 (a) and (b) atomic and band structures of a CNT with a parallel GB, respectively, (c) and (d) atomic and band structures of a CNT with a perpendicular GB, respectively (After [62]).

### 2.4 Modeling and characterization of electrical properties

Dispersing CNTs into an insulating polymer transform it into an electrical conductive material due to the formation of conductive pathways of percolating CNT networks spanning through the composite [63,64]. These conductive polymeric based composites are very good candidates for several engineering applications including structural health monitoring, electromagnetic interference shielding of electronics, and lightning strike protection for aerospace vehicles [2,65]. In general, the electric charge is transmitted inside the composite through percolating CNT networks in two forms: (i) the ballistic transport of electrons along CNTs, and (ii) the electron tunneling between sufficiently close CNTs (minimum distance ≤ maximum tunneling distance) [66-68]. Figure 2.10 shows a percolating network formed in a RVE filled with randomly dispersed SWCNTs.
Figure 2.10 (a) An atomistic model of a RVE reinforced with randomly dispersed SWCNTs, (b) an equivalent representation of the CNTs as 3D sticks, and (c) the percolating CNTs network (the blue arrows representing the direction of the electric current).

Several experimental, theoretical, and numerical studies were conducted to investigate the electrical and the percolation properties of CNT-reinforced composites [63,66,69]. The electrical conductivity was found to increase abruptly when the CNT concentration reached a specific volume fraction (i.e. the percolation threshold) indicating the formation of at least a single percolating CNTs network [70]. The electrical conductivity continued to increase with increasing the CNT volume fraction due to the formation of conductive pathways. The relationship between the conductivity and CNT concentration can be described by the percolation theory, as shown in Figure 2.11(a).

Figure 2.11 (a) The electrical conductivity of a CNT-polymer composite as a function of the CNT volume fraction (After [70]), and (b) a schematic representation of three connected CNTs and an equivalent electric circuit formed from intrinsic and tunneling resistances.
Monte-Carlo simulations were used in previous studies to determine the percolation probability and the effective electrical conductivity of CNT-epoxy composites [69,71]. In order to simulate the percolating CNT networks inside the composite, an equivalent electric circuit was constructed by modeling the randomly dispersed CNTs as cylindrical rods, as shown in Figs. 2.10(b). The intersection between two rods was assumed to exist if the minimum distance between them was less than the maximum tunneling distance [71,72]. The percolating CNTs network was built by checking the existence of a continuous path between any two opposite sides of the RVE (see Fig. 2.10(c)). Once the percolating CNT network was identified, an equivalent resistance network was then developed by transforming the percolating CNT network into an equivalent resistors circuit [71], as shown in Fig. 2.11(b). The electrical resistances in the percolating network exist in two types: the intrinsic resistance $R_{CNT}$ and the tunneling resistance $R_{tunnel}$:

$$R_{CNT} = \rho_{CNT} \frac{4L_{CNT}}{\pi D^2}$$

and

$$R_{tunnel} = \frac{h}{2e^2} \cdot \frac{1}{MT} \quad (2.1)$$

where $\rho_{CNT}$ is the CNT resistivity, $L_{CNT}$ is the length of the CNT segment between the two contact points, $T$ is the transmission probability, and $M$ is the total number of conduction channels, $e$ is the electron charge, and $h$ is Planck’s constant. A matrix is then created for each resistor element in the CNT network as follows:

$$\begin{bmatrix} I_i^e \\ I_j^e \end{bmatrix} = \begin{bmatrix} K_{ij}^e \end{bmatrix} \begin{bmatrix} v_i \\ v_j \end{bmatrix} = \begin{bmatrix} 1 \\ -1 \\ -1 \\ 1 \end{bmatrix} \begin{bmatrix} v_i \\ v_j \end{bmatrix} \quad (2.2)$$

where $i$ and $j$ refer to the end nodes of the resistor, $I^e$ is the electric current passing through this node, $v$ is the nodal voltage, $K^e$ is the element conductance, and $R^e$ is the element resistance. The local matrices for all resistors are then assembled to build the resistor matrix for the entire percolating network, $K$, according to Kirchhoff’s current law [73]:

$$I = KV \quad (2.3)$$

where $I$ and $V$ are vectors representing external input current and voltage of all nodes. The global coefficient matrix $K$ is defined by:

$$K = \sum_{e=1}^{m} [K_{ij}^e] \quad (2.4)$$
where m is the number of resistances in the percolating network assembled matrix. The effective resistance of the percolating networks could be obtained by solving the matrix representing the assembled electrical resistances with Cholesky decomposition algorithm for sparse matrices [71].

**2.5 Modeling and characterization of electromechanical coupling**

The electrical conductivity of CNT-reinforced composite films changes with the applied load, indicating a strong strain sensing capability and hence being a potential candidate for structural health monitoring applications [74]. The electrical current in these films is transmitted through networks of percolating CNT networks spanning through the material and connecting the two sides of the conductive films [69]. The electromechanical behavior of the nanocomposite is attributed to: (i) the change in the intrinsic resistances of the deformed CNTs due to the shift in the G band [75], and (ii) the change in the tunneling resistances between adjacent CNTs in percolating networks in response to CNTs dislocations during loading [76].

The electromechanical coupling of CNT-reinforced composites has been investigated in the literature by a number of experimental [77-82], analytical [83-87], and numerical studies [88-90]. Experimentally, Wichmann et al. [91] developed strain sensor from a MWCNT/epoxy composite that is capable of measuring bending deflection by generating a gradient in electrical conductivity throughout the composite block. Their measurements showed a nearly linear relationship between the sensor resistance and the applied mechanical strain. Böger et al. [92] developed a conductive adhesive from epoxy matrix reinforced with CNTs to monitor the condition of glass fiber reinforced composites subjected to tensile and fatigue loadings. Their results showed that the developed monitoring method had a higher sensitivity compared to other damage sensing techniques. Thostenson and Chou [93] developed an in situ sensor for damage detection and evolution in advanced fiber composites during cyclic loads by utilizing the piezoresistivity of CNT-based adhesives. The variation of the electrical resistance showed a clear indication of the crack opening and closure under the cyclic loading, as shown in Fig. 2.12.

Park et al. [94] investigated the strain-dependent electrical resistance of polyethylene oxide reinforced with different volume fractions of MWCNTs. The resistance-strain curves consisted of
an initial linear region followed by nonlinear region. The slope and size of each region was found to depend on the CNT volume fraction. Kang et al. [95] managed later to develop a SWCNT/polyamide composite with piezoresistive coefficient significantly higher than metallic strain gauges. Experimental results presented by Yasuoka et al. [78] showed that the strain dependent electrical resistance of CNT-reinforced composites decreases nonlinearly with the increase of the CNT concentration. Oliva-Avilés et al. [96] managed to improve the electrical conductivity and piezoresistive properties significantly by aligning the dispersed CNTs in the composite by applying an external electric field. The gauge factor of the resulting composite reached 3.2 which is higher than those reported for common metal foil gages. CNTs were successfully incorporated with polyurethane elastomer to develop a new nanocomposite sensor for measuring tensile strains up to 400% [97]. More recently, Dai et al. [81] developed a damage location and size detection technique of aramid fabric-based composite using a 2D mapping of the electrical conductivity changes in a CNT-epoxy coating.

![Figure 2.12](image)

**Figure 2.12** (a) The change in the electrical resistance under cyclic loading, (b) SEM image showing the formation of a microscale crack in a 90° ply, and (c) SEM image of the protruding CNTs from the matrix at the crack surface (After [93]).

Furthermore, different modeling schemes were developed over the last decade to study the electromechanical coupling behavior in CNT reinforced composites and adhesives [94,98]. For example, Park et al. [94] developed a simplified model to calculate the change in resistance of a CNT-polymer film under tensile load. In their model, they assumed that the tunneling resistance has an impact only at higher strains and CNTs are mainly overlapping at the contact locations. Amore advanced model was developed by Li et al. [98] to investigate the mechanism of damage
sensing in glass fiber composites reinforced with CNTs. In their two-dimensional (2D) electromechanical model, the percolating CNT networks were considered as pseudo 3D networks formed from resistors representing tunneling resistances between the embedded CNTs, as shown in Fig. 2.13(a) and (b). The electrical conductivity of the system was obtained using the FE method for electrical circuits, while the structural response of the system was determined with a 2D FE analysis. The crack onset and propagation were monitored in the FE model by considering a damage criterion based on the maximum principal tensile stress. The resulting change in the electrical conductivity indicated the damage initiation on the cross-ply (see Fig. 2.13(c)).

![Figure 2.13](image)

**Figure 2.13** (a) A percolating CNTs network in the fiber composite, (b) a schematic diagram of the equivalent resistor network, and (c) variation of the tensile load and the electric resistance with the applied tensile strain (After [98]).

Anand et al. [83] developed a mathematical model based on Bruggeman’s effective medium theory to study the nonlinear electromechanical coupling of CNT-epoxy composite thin films. They attributed the nonlinear strain-dependent resistance behavior to the increase in the effective energy band-gap of the composite due to the relatively large strains in the polymer matrix. Shindo et al. [85] developed an analytical model to predict the resistance change resulted from crack propagation in CNT-reinforced composites. The electrical current was assumed in their model to be transmitted through conductive parallel pathways formed from the percolating CNTs (see Fig 14(a)). The change in the conductivity during the fracture was assumed to originate from the loss of the conductive pathways passing through the crack surface (see Fig. 2.14(b)). More advanced models were developed later in Refs. [99,100] to study the piezoresistive behavior of CNT reinforced polymers by combining a 3D resistor network model and a fiber reorientation model to update the location and orientation of each CNT in the percolating network under different
strain levels, as shown in Fig. 2.15. The electrical conductivity of the strained RVE was then calculated and the obtained relationship between the resistance and the applied strain was used to calculate the piezoresistive coefficient of the sensor.

![Figure 2.14](image1.png)  
**Figure 2.14** (a) Transformation of the percolating networks inside the composite into equivalent parallel pathways, and (b) a schematic representation of the break down of conductive pathways in the single-edge cracked specimen (After [85]).

![Figure 2.15](image2.png)  
**Figure 2.15** A schematic illustration of randomly oriented CNTs in a polymer matrix where the locations of the CNTs ends are updated under the applied strain (After [100]).

### 2.6 References

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PART I

Multiscale Modeling of Mechanical Properties of CNT-Reinforced Polymer Composites

Summary: In the first part of this thesis, we investigated the mechanical properties of pristine and defective CNTs, pure polyethylene and epoxy polymers, and their nanocomposites using several analytical and numerical techniques. The conducted work in this subject is presented in the next four chapters. As this is a non-traditional format paper-based thesis, each chapter has been written in the form of a journal paper. In Chapter 4, a novel multiscale modeling technique for CNT-reinforced polymer composites was developed based on MD simulations and micromechanical modeling technique. The stiffness tensor of an effective fiber consists of a CNT surrounded by a layer of cross-linked epoxy resins were first obtained using MD simulations with the constant-strain energy minimization method. The obtained elastic moduli at the nanoscale level were then scaled up to the bulk level using the Mori-Tanaka micromechanical method. This model was extended in Chapter 5 to account for CNT morphology, agglomeration, and orientations on both nanoscale and bulk elastic properties of the nanocomposite. In Chapter 6, we present a large-scale atomistic study, which is the first of its type, of a CNT-reinforced polyethylene composite with realistic microstructure. RVEs filled with straight and wavy CNTs with aspect ratios up 500 and different bundle sizes were modeled using MD simulations. The developed one-million atoms size systems were able to capture accurately the bulk properties of the nanocomposite and avoided the inherent limitations in existing multiscale models. In chapter 6, we extended our work to consider defective CNTs and CNT junctions. An extensive MD study was conducted to investigate the effect of grain boundaries on mechanical and fracture properties of polycrystalline CNTs. The output results from this investigation will be used in the future as an input to the coupled electromechanical model developed in this thesis to investigate multifunctional properties of polymer composites reinforced by CNTs with different kinds of defects.
Chapter 3.
**Paper #1: Multiscale modelling of carbon nanotube epoxy composites**

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### 3.1 Abstract

In this article, a multiscale modeling technique is developed to determine the effective elastic moduli of CNT-reinforced epoxy composites containing either well-dispersed or agglomerated carbon nanotubes (CNTs). Two aspects of the work are accordingly examined. In the first, molecular dynamics simulations are carried out to determine the atomic-level elastic properties of a representative volume element (RVE) comprised of either epoxy polymer or transversely isotropic CNT-epoxy composite. To study the effect of agglomeration of CNTs on the bulk elastic properties of the nanocomposite, CNT bundles of different sizes were considered. A constant-strain energy minimization method is used to determine the elastic coefficients of the RVEs. In the second, the Mori-Tanaka method is used to scale up the properties of the atomic structure to the microscale level, and the outcome is used to investigate the effect of orientations and agglomeration of CNTs on the bulk elastic properties of the nanocomposite. Our results reveal that as the number of CNTs in the bundle increases, the effective elastic properties of the nanocomposite decrease at the same CNT volume fraction.

**Keywords:** Multiscale modeling, Molecular dynamics, Micromechanics, Nanocomposites, Carbon nanotube, Orientation, Agglomeration, Effective elastic properties
3.2 Introduction

Owing to their remarkable mechanical and physical properties, CNTs [1] have emerged as one of the most promising reinforcements to tailor the properties of polymer-based nanocomposites [2–5]. Due to these exceptional properties, it is believed that few weight percentages of CNTs can significantly improve the mechanical properties of CNT-based composites. A significant number of experimental and numerical studies have been conducted to study the effective elastic properties of CNT-reinforced polymer composites. An earlier attempt was made by Schadler et al. [6] to measure the mechanical properties of CNT-reinforced polymer composite. They reported that Young’s modulus in tension and compression can be improved by as much as 20% and 45% at 5 wt% of CNTs. Allaoui et al. [7] achieved significant enhancement in the mechanical properties of CNT–reinforced epoxy composite. In their study, Young’s modulus and the yield strength were doubled for the nanocomposite with 1 and 4 wt% of multi-walled CNTs, respectively, compared to the pure epoxy matrix. Park et al. [8] synthesized a polyimide composite reinforced with CNTs, and reported improved mechanical, thermal, electrical and optical properties. Gou et al. [9] investigated the interfacial bonding of CNT-epoxy composites using a combination of computational and experimental methods. The uniform dispersion and good interfacial bonding of CNTs in the epoxy resin resulted in a 250–300% increase in the storage modulus with the addition of 20–30 wt% of CNTs. Li et al. [10] studied the mechanical properties of CNT–reinforced epoxy composite. At 5 wt% of CNTs, Young’s modulus of the nanocomposite increased from 4 to 7 GPa. Meguid and Sun [11] showed that the homogeneous dispersion of CNTs in the epoxy matrix can improve the tensile and shear strength of the resulting synthesized nanocomposite. However, at higher CNT concentrations the mechanical properties of the nanocomposite were found to deteriorate due to the formation of CNT agglomerates, which act as stress concentrators. Qu et al. [12] fabricated CNT composite films with a specifically designed amine-terminated polyimide and obtained high quality, optically transparent, and homogeneous films.

Additionally, molecular dynamics (MD) simulations have also been used to study the mechanical properties of CNT-reinforced composites. For example, Frankland et al. [13] used MD simulations to calculate the longitudinal and transverse Young’s moduli of polymer nanocomposite reinforced by long and short CNTs. Griebel and Hamaekers [14] estimated the
elastic moduli of single walled carbon nanotube (SWCNT)-PE composites using MD simulations. Their MD results show an excellent agreement with the results predicted by rule-of-mixtures. Al-Ostaz et al. [15] carried out MD simulations to estimate the elastic properties of SWCNT, interfacial bonding, polyethylene matrix and composites with aligned and randomly distributed SWCNTs. Grujicic et al. [16] studied the effect of chemical functionalization on the mechanical properties of multi-walled CNT-vinyl ester epoxy composites using MD simulations. Introduction of covalent bonds between the CNT and the polymer results in significant improvements in the transverse elastic properties of the nanocomposite. Yang et al. [17] developed a multiscale model considering the CNT size and weakened bonding effects of the CNT-polymer interface on the effective elastic stiffness of CNT-polymer composite by using MD simulations and a modified multi-inclusion micromechanics model. Recently, Khare et al. [18] used amido-amine functionalized CNTs that form covalent bonds with cross-linked epoxy matrices to investigate the role of the CNT-matrix interphase in the enhancement of mechanical and thermal properties in these nanocomposites.

Despite the remarkable elastic properties of CNTs, the reported results in the literature show a limited enhancement in the effective elastic properties of their nanocomposites. There exist numerous reasons for this discrepancy; including, poor dispersion of the CNTs, agglomeration and aggregation leading to inferior properties, poor interfacial properties resulting in limited stress transfer and load sharing. Other parameters that influence the resulting properties of nanocomposite include the quality of CNTs used, their purities, geometry and aspect ratios as well as orientation within the nanocomposite [19]. For instance, micro-Raman spectroscopy was used by Ajayan et al. [20] to measure the local elastic behavior of individual SWCNT bundles in epoxy-based nanocomposite. They noticed that the efficiency of the stress transfer and hence the enhancement of the mechanical properties is lower than expected due to the sliding of the CNTs in the agglomerated bundles. More recently, in order to investigate how the CNT content and arrangement affect the characteristics of the system, molecular models of unidirectional nanocomposite comprised of different volume fractions of CNTs were studied by Jiang et al. [21].

Due to the technical difficulties inherent in the preparation and testing of CNT-reinforced polymer composites, different multiscale modeling techniques have been developed over the last decade to predict the properties of these nanocomposites at the microscale level. In general, multiscale
modeling of CNT-reinforced polymer composites is achieved in two consecutive steps. At the nanoscale, the atomic structures of the CNT and the surrounding epoxy matrix cannot be considered as a continuum medium, and the bulk elastic properties can no longer be obtained using the traditional continuum mechanics approaches. Therefore, in the first step the properties of an effective fiber representing long or short CNT embedded inside a unit cell surrounded by polymer molecules are evaluated using either atomistic based continuum (ABC) technique or molecular dynamics (MD) simulation. In the second step, micromechanics method or finite element technique can then be used to calculate the bulk effective properties of the composite at the microscale [5, 17, 22–25].

The performance of CNT-polymer composites is greatly influenced by the orientations and agglomeration of CNTs in polymers [11, 19, 20, 22, 25–28]. Due to the high-surface-to-volume ratio, CNT agglomerates in the synthesized composite leads to nanocomposite with very low elastic properties. On the other hand, the alignment of the dispersed CNTs was found to enhance the elastic modulus along the alignment direction [19]. However, limited work has been reported on MD simulations of CNT bundle-based composites compared to the researches on well-dispersed CNT-reinforced composites. In addition, most of the MD studies on CNT-based composites utilized thermoplastic polymers, such as polyethylene, polypropylene and PMMA as a matrix phase [13, 14, 17]. On the other hand, MD studies utilizing thermoset polymer as a matrix phase are limited in the literature. To the best of our knowledge, there has been no multiscale modeling study for investigating the influence of CNT agglomeration on the effective elastic properties of CNT-reinforced epoxy composites. It is therefore the objective of this paper to develop a multiscale model to determine the bulk elastic properties of CNT-reinforced epoxy composite. In the current study, CNT bundles are considered as a special case of CNT agglomerates. The proposed multiscale model is developed in two steps. In the first, MD simulations were used to determine the transversely isotropic elastic properties of RVEs containing either an individual CNT or a bundle of CNTs embedded in epoxy. In the second, the determined elastic moduli of the RVEs were used to determine the influence of orientations and agglomeration of CNTs on the bulk elastic properties of the nanocomposite using Mori-Tanaka model.
3.3 Multiscale Modeling Procedure

In this Section, a multiscale model is developed in two steps. In the first, we use MD simulation to determine the isotropic stiffness tensor of the RVE filled with the epoxy material and the transversely isotropic stiffness tensor of the RVEs representing either an individual CNT or a bundle of CNTs embedded in an epoxy matrix. In the second, considering the nanocomposite RVE as the reinforcement and the epoxy polymer as the matrix phase, the effective elastic moduli of the nanocomposite are scaled up from the nanoscale to the microscale using the Mori-Tanaka method. Fig. 3.1 shows the steps involved in the hierarchical multiscale model.

![Diagram](image)

**Figure 3.1** Modeling steps involved in the developed multiscale model.

3.3.1 MD Simulations

In the present study, MD simulations were conducted to determine the equivalent elastic properties of the composite constituents at the atomic scale. MD simulations offer an appropriate and effective means to deal with large systems and relatively longer simulation times. All MD simulations runs were conducted with large-scale atomic/molecular massively parallel simulator (LAMMPS) [29] by using the consistent valence force field (CVFF) [30]. This force field has been used by other researchers to predict the mechanical properties of CNTs and epoxy polymers [31–33]. Conjugate gradient algorithm was used to minimize the total potential energy of the initial configurations, while velocity Verlet algorithm was used to integrate the equations of motion in all MD simulations. Periodic boundary conditions were imposed on all directions of the MD unit cells. We have only considered non-bonded interactions between the atoms of the embedded CNTs and the surrounding epoxy. In the simulations, the non-bonded interactions
between the atoms are represented by van der Waals (vdW) interactions and Coulombic forces. The cut-off distance for the non-bonded interaction was set to 14.0 Å [34]. Determination of the atomic-level elastic properties of the pure epoxy and the nanocomposite RVE was accomplished by straining the MD unit cells followed by constant-strain energy minimization. The averaged stress tensor of the MD unit cell is defined in the form of virial stress [35]; as follows

$$\sigma = \frac{1}{V} \sum_{i=1}^{N} \left( \frac{m_i v_i^2}{2} + F_i r_i \right)$$ (3.1)

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

**Modeling of Pure Epoxy**

To model the surrounding matrix, we used a specific two-component epoxy material based on a diglycidyl ether of bisphenol A (DGEBA) epoxy resin and triethylene tetramine (TETA) curing agent, which is typically used in the aerospace industry (see Fig. 3.2).

![Molecular structures of (a) epoxy resin (DGEBA) and (b) curing agent.](image)

**Figure 3.2** Molecular structures of (a) epoxy resin (DGEBA) and (b) curing agent.

During the curing process, the hydrogen atoms in the amine groups of the hardener (TETA) react with the epoxide groups of the resin (DGEBA) forming covalent bonds, which result in a highly cross-linked epoxy structure [36], as depicted in Fig. 3.3.

† A detailed description of the governing parameters of MD simulations are provided in Appendix 1.
Figure 3.3 Steps used in the preparation of the polymer matrix (a) cross-linked structure, (b) distorted structure in the 3D unit cell, (c) five 80:40 cross-linked structure randomly placed in a simulation box of size 150 Å × 150 Å × 150 Å, and (d) the equilibrated system in a simulation box of size 61 Å × 61 Å × 61 Å after 25 volume reduction steps.

The resin/curing agent weight ratio in the epoxy polymer was set to 2:1 in order to achieve the best elastic properties. [25] The cross-linked polymer structure consisted of 80 DGEBA molecules cross-linked with 40 molecules of curing agent TETA (see Fig. 3.3(a)). The cross-linked structure was utilized to form a 3D structure, as shown in Fig. 3.3(b). This cross-linked epoxy structure was then used to build the epoxy system in the subsequent MD simulations for both neat epoxy and CNT-epoxy composite. The neat epoxy model was generated by randomly placing 5 cross-linked structures in a cubic simulation box of size 150 Å × 150 Å × 150 Å to form a system containing 400 chains of DEGBA and 200 chains of TETA [37, 38], as shown in Fig. 3.3(c). The total number of atoms in the simulation box is 25300. In the current work, the volumetric bulk modulus (K)
and shear modulus \((G)\) of the cross-linked epoxy were determined by applying the volumetric and three-dimensional shear strains, respectively [38]. The main steps involved in determining the elastic moduli of pure epoxy were as follows:

**Step 1 (volume reduction):** The simulation box was compressed gradually through 25 steps from its initial size of \(150\,\text{Å} \times 150\,\text{Å} \times 150\,\text{Å}\) to the targeted dimensions of \(61\,\text{Å} \times 61\,\text{Å} \times 61\,\text{Å}\) (see Fig. 3.3d). At each stage, the atoms coordinates were remapped to fit inside the compressed box, then a minimization simulation was performed to relax the coordinates of the atoms. The system was considered to be optimized once the change in the total potential energy of the system between subsequent steps is less than \(1.0 \times 10^{-10}\) kcal/mol. The optimized system was then equilibrated at room temperature in the constant temperature and volume canonical (NVT) ensemble over 100 ps by using a time step of 1 fs.

**Step 2 (density adjustment):** The compressed system was equilibrated for another 200 ps in the isothermal–isobaric (NPT) ensemble at 300 K and 1 atm to generate an epoxy system with the correct density and to reduce the induced residual stresses due to the volume reduction. This equilibration step resulted in an equilibrated amorphous structure with an average density of \(1.0\,\text{g/cm}^3\). At the end, the structure is again equilibrated for 200 ps in the NVT ensemble at 300 K.

**Step 3 (elastic constants):** The simulation box was volumetrically strained in both tension and compression to determine the bulk modulus by applying equal strains along all three axes. The bulk modulus was calculated by:

\[
K = \frac{\sigma_h}{\varepsilon_v}
\]  

(3.2)

where \(\varepsilon_v\) and \(\sigma_h\) are the volumetric strain and the averaged hydrostatic stress, respectively. The average shear modulus was determined by applying equal shear strains on the simulation box in \(xy, xz,\) and \(yz\) planes. The shear modulus was calculated by:

\[
G = \frac{\tau_{ij}}{\gamma_{ij}}, \quad i \neq j
\]  

(3.3)

where \(\tau_{ij}\) and \(\gamma_{ij}\) denote the averaged shear stress and shear strain, respectively.

In all simulations, strain increments of 0.25% were applied along a particular direction by uniformly expanding or shearing the simulation box and updating the atoms coordinates to fit
within the new dimensions. After each strain increment, the MD unit cell was equilibrated using the NVT ensemble at 300 K for 10 ps. Then, the stress tensor is averaged over an interval of 10 ps to reduce the effect of fluctuations. These steps were repeated in the subsequent deformation increments. The procedure was stopped when the total strain reached up to 2.5%. Based on the calculated bulk and shear moduli, Young’s modulus (E) and Poisson’s ratio (ν) were determined as follows:

\[
E = \frac{9KG}{3K+G} \quad \text{and} \quad \nu = \frac{3K-2G}{2(3K+G)}
\]  

(3.4)

The predicted elastic properties of the epoxy using MD simulations are summarized in Table 3.1. These moduli are consistent with the experimentally measured moduli of a similar epoxy [39, 40].

### Table 3-1 Elastic moduli of the epoxy material.

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>bulk modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD simulations</td>
<td>3.2</td>
<td>1.1</td>
<td>4.9</td>
<td>0.39</td>
</tr>
<tr>
<td>Experimental work [39]</td>
<td>2.9</td>
<td>1.0</td>
<td>4.4</td>
<td>0.35</td>
</tr>
</tbody>
</table>

#### CNT-Epoxy Interface Layer Thickness

The structure of the epoxy matrix at the vicinity of the CNT surface differs from the bulk epoxy due to the formation of an ultra-thin epoxy layer at the CNT-epoxy interface [41]. This ultra-thin layer consists of a highly packed crystalline polymer, which has higher elastic properties than the amorphous bulk polymer [41–43]. Therefore, in order to obtain the actual CNT-epoxy properties, the size of the RVE must be large enough to incorporate the interface layer. Armchair (5, 5) CNTs were used in the present work for both individual and agglomerated CNTs reinforcements. The cylindrical molecular structure of the CNT is treated as an equivalent solid cylindrical fiber [5, 22, 44, 45] for determining its volume fraction in the nanocomposite RVE,

\[
v_{CNT} \approx f_n N_{CNT} \frac{\pi (D_{CNT} + h_{vdW})^2 L_{CNT}}{4 V_{cell}}
\]  

(3.5)

where \( D_{CNT} \) and \( L_{CNT} \) denote the respective diameter and length of a CNT; \( h_{vdW} \) is the vdW equilibrium distance between a CNT and the surrounding polymer matrix; \( N_{CNT} \) is the number of
CNTs in the bundle; $f_n$ is a factor based on the shape of the bundle of CNTs; and $V_{cell}$ is the volume of the RVE.

In order to determine the thickness of the interface layer, we performed MD simulations for a system consisting of a CNT of length 76.0 Å surrounded by 4 cross-linked 80:40 epoxy structures. The initial size of the periodic RVE was 150 Å × 150 Å × 150 Å. Subsequently, the volume of the simulation box was gradually reduced to 60 Å × 60 Å × 76 Å and equilibrated using the same steps as adopted in the pure epoxy case. Fig. 3.4 shows the simulation box of the nanocomposite system prior to and post equilibration. Fig. 3.5 shows the radial distribution function (RDF) of the epoxy atoms that surround the embedded CNT after the equilibration.

![Figure 3.4](image)

**Figure 3.4** The simulation box used to study the interface layer: (a) before volume reduction, and (b) after equilibration.

The variation of the RDF along the radial direction represents the change of the epoxy structure in the vicinity of the embedded CNT. It may be observed from Fig. 3.5 that the RDF of epoxy atoms is zero at the radial distance of 0.56 nm and reaches its maximum value of 160 atoms/nm$^3$ at the radial distance of 0.77 nm. Then, it starts to fluctuate around an average value of 110 atoms/nm$^3$. This result indicates that the value of the vdW equilibrium distance $h_{vdW}$ is ~2.75 Å and the thickness of CNT-epoxy matrix interface layer is ~3.0 Å. The obtained values of the
interface thickness and the equilibrium separation distance were used to select the appropriate
RVE sizes and in calculating the actual volume fraction of the embedded CNTs in the RVE.

**Figure 3.5** RDF of the epoxy atoms around the embedded CNT.

**MD Simulations of CNT-Reinforced Epoxy Composite**

It is difficult to uniformly disperse CNTs in the matrix during the fabrication process and the
situation becomes more challenging at high CNT loadings. This is attributed to the fact that CNTs
have a tendency to agglomerate and aggregate into bundles due to their high surface energy and
surface area [46]. Therefore, it is necessary to investigate the influence of CNT bundling on the
bulk elastic properties of their nanocomposites. For such an investigation, three RVEs were
constructed to represent an epoxy matrix containing a: (i) single CNT, (ii) bundle of three CNTs,
and (iii) bundle of seven CNTs. Such RVEs are shown in Fig. 3.6. The initial distance between
the adjacent CNTs in the bundle was taken to be 3.4 Å (see Fig. 3.7), which is the intertube
separation distance in multi-walled CNTs.
The RVEs are assumed to be transversely isotropic with the $3$–axis being the axis of symmetry. Therefore, only five independent material constants are required to fully define the elastic stiffness matrix. The constitutive relationship of the transversely isotropic RVE is given by:
\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & (C_{11} - C_{12})/2
\end{bmatrix} \begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{bmatrix} \tag{3.6}
\]

where \( \sigma_{ij} \) and \( \varepsilon_{ij} \) are the respective stress and strain components with \((i, j = 1, 2, 3, 4, 5, 6)\) and \( C_{ij} \) represents the elastic coefficients of the RVE. A series of MD simulations were carried out to determine the elastic moduli of the RVEs. The simulation box in each case was constructed by randomly placing the cross-linked epoxy structures around the CNT bundle. The size of the RVE in each case was adjusted in such a way that the CNT volume fraction in it remains constant at 6.5%, irrespective of the number of CNTs, as shown in Fig. 3.6. The details of the three RVEs are summarized in Table 3.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Single CNT</th>
<th>Bundle of three CNTs</th>
<th>Bundle of seven CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT type</td>
<td>(5, 5)</td>
<td>(5, 5)</td>
<td>(5, 5)</td>
</tr>
<tr>
<td>Number of CNTs</td>
<td>1</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>Length of a CNT (Å)</td>
<td>73</td>
<td>73</td>
<td>76</td>
</tr>
<tr>
<td>CNT volume fraction</td>
<td>6.5%</td>
<td>6.5%</td>
<td>6.5%</td>
</tr>
<tr>
<td>RVE dimensions (Å(^3))</td>
<td>31\times31\times76</td>
<td>55\times55\times76</td>
<td>88\times88\times76</td>
</tr>
<tr>
<td>Total number of DEGBA molecules</td>
<td>120</td>
<td>320</td>
<td>960</td>
</tr>
<tr>
<td>Total number of TETA molecules</td>
<td>60</td>
<td>160</td>
<td>480</td>
</tr>
<tr>
<td>Total number of atoms</td>
<td>7836</td>
<td>21116</td>
<td>62028</td>
</tr>
</tbody>
</table>

To determine the five elastic constants, the RVEs were subjected to five different tests: longitudinal tension, transverse tension, in-plane tension, in-plane shear and out of-plane shear. The steps involved in the MD simulations of the RVEs are the same as adopted in the case of pure epoxy. The boundary and loading conditions that have been applied to the RVE to determine the corresponding five independent elastic coefficients of the RVE are listed in Table 3.3. A series of MD simulations were carried out to determine the elastic properties of transversely isotropic RVEs reinforced with either an individual CNT or bundles of CNTs. Fig. 3.8 demonstrates close views of the equilibrated RVEs. Table 3.4 summarizes the outcome of the MD simulations.
Table 3-3 Effective elastic coefficients of the RVEs and corresponding displacement fields.

<table>
<thead>
<tr>
<th>Elastic coefficients</th>
<th>Applied strains</th>
<th>Applied displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>$\varepsilon_{11} = \varepsilon$</td>
<td>$u_1 = e x_1$</td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>$\varepsilon_{33} = \varepsilon$</td>
<td>$u_3 = e x_3$</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>$\varepsilon_{23} = \varepsilon/2$</td>
<td>$u_2 = \frac{e}{2} x_3, \ u_3 = \frac{e}{2} x_2$</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>$\varepsilon_{12} = \varepsilon/2$</td>
<td>$u_1 = \frac{e}{2} x_2, \ u_2 = \frac{e}{2} x_1$</td>
</tr>
</tbody>
</table>

$K_{12} = \frac{C_{11} + C_{12}}{2}$

$\varepsilon_{11} = \varepsilon_{22}$

$u_1 = e x_1, u_2 = e x_2$

Figure 3.8 Snapshots of the transverse cross-sections of the MD unit cells containing $a$: (a) single CNT, (b) bundle of three CNTs and (c) bundle of seven CNTs.

Table 3-4 Material properties of the nanocomposite RVE containing either an individual CNT or its bundle.

<table>
<thead>
<tr>
<th>RVE</th>
<th>CNT volume fraction in RVE ($v_{CNT}$)</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{13}$ (GPa)</th>
<th>$C_{33}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$C_{66}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single CNT</td>
<td>6.5%</td>
<td>11.8</td>
<td>.71</td>
<td>5.6</td>
<td>47.35</td>
<td>3.16</td>
<td>2.35</td>
</tr>
<tr>
<td>Bundle of three CNTs</td>
<td></td>
<td>10.5</td>
<td>6.6</td>
<td>4.5</td>
<td>37.4</td>
<td>1.89</td>
<td>1.95</td>
</tr>
<tr>
<td>Bundle of seven CNTs</td>
<td></td>
<td>9.1</td>
<td>5.9</td>
<td>3.5</td>
<td>29.2</td>
<td>1.48</td>
<td>1.6</td>
</tr>
</tbody>
</table>

It may be observed from the results that the elastic properties of the RVEs are significantly higher than those of the neat epoxy. It is also clear from the results that the CNT agglomeration reduces the reinforcing effect of the embedded CNTs, which eventually degrades the bulk elastic moduli of the nanocomposites. The axial elastic coefficients ($C_{33}$) of the RVEs containing bundles of
three and seven CNTs decreased by some 21% and 38.5%, respectively, as compared with the RVE containing an individual CNT. The CNT agglomeration is also found to affect the transverse elastic coefficients of the RVEs. For example, the transverse elastic coefficient ($C_{11}$) of the RVEs containing bundles of three and seven CNTs decreased by 11.0% and 22.9%, respectively, compared with the RVE containing an individual CNT. Each RVE will be used as an effective fiber in the micromechanical model to calculate the effective elastic moduli of the nanocomposite at the microscale level (see Fig. 3.1).

### 3.3.2 Micromechanics Model

In this section, the elastic moduli of the pure epoxy and the nanocomposite RVE obtained from the MD simulations are used as an input to the micromechanical model in order to determine the bulk elastic properties of the nanocomposite. With this process firmly established in several studies [5, 17, 22–25], the Mori-Tanaka model [47, 48] can be developed by utilizing the transversely isotropic elastic properties of the nanocomposite RVE and the isotropic elastic properties of the pure epoxy matrix. In case of two-phase composite, where the inhomogeneity is randomly orientated in the three-dimensional space, the following relation can be used to determine the effective stiffness tensor $[C]$ of the nanocomposite:

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

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

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

where $[C^m]$ and $[C^{RVE}]$ are the stiffness tensors of the epoxy matrix and the RVE, respectively; $[I]$ is an identity matrix; $v_m$ and $v_{RVE}$ represent the volume fractions of the epoxy matrix and the RVE, respectively; and $[S^{RVE}]$ indicate the Eshelby tensor†. The specific form of the Eshelby tensor for the RVE inclusion given by Qiu and Weng [49] is utilized herein. It may be noted that the elastic coefficient matrix $[C]$ directly provides the values of the effective elastic properties of the nanocomposite, where the RVE is aligned with the 3–axis.

† The components of the Eshelby tensor are provided in Appendix 2.
In case of random orientations of CNTs, the terms enclosed with angle brackets in Eq. (3.7) represent the average value of the term over all orientations defined by transformation from the local coordinate system of the RVE to the global coordinate system. The transformed mechanical strain concentration tensor for the RVEs with respect to the global coordinates is given by

$$
\tilde{A}_{ijkl} = t_{ip} t_{jq} t_{kr} t_{ls} A_{pqrs}
$$

(3.9)

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

- $t_{11} = \cos \phi \cos \psi - \sin \phi \cos \gamma \sin \psi,$
- $t_{12} = \sin \phi \cos \psi + \cos \phi \cos \gamma \sin \psi,$
- $t_{13} = \sin \psi \sin \gamma,$
- $t_{21} = -\cos \phi \sin \psi - \sin \phi \cos \gamma \cos \psi,$
- $t_{22} = -\sin \phi \sin \psi + \cos \phi \cos \gamma \cos \psi,$
- $t_{23} = \sin \gamma \cos \psi,$
- $t_{31} = \sin \phi \sin \gamma,$
- $t_{32} = -\cos \phi \sin \gamma,$
- $t_{33} = \cos \gamma$

Consequently, the random orientation average of the dilute mechanical strain concentration tensor $\langle [A] \rangle$ can be determined by using the following equation [50]:

$$
\langle [A] \rangle = \frac{\int_{-\pi}^{\pi} \int_{-\pi/2}^{\pi/2} \int_{-\pi}^{\pi} [\tilde{A}](\phi, \gamma, \psi) \sin \gamma \, d\phi \, d\gamma \, d\psi}{\int_{-\pi}^{\pi} \sin \gamma \, d\phi \, d\gamma \, d\psi}
$$

(3.10)

where $\phi$, $\gamma$, and $\psi$ are the Euler angles as shown in Fig. 3.9. It may be noted that the averaged mechanical strain concentration tensors given by Eqs. (3.8) and (3.10) are used for the cases of aligned and random orientations of CNTs, respectively, in Eq. (3.7).

![Figure 3.9 Relationship between the local coordinates (1, 2, 3) of the RVE and the global coordinates (1`, 2`, 3`) of the bulk composite.](image)
3.4 Results and Discussion

In this Section, the results of the developed multiscale model are compared with the existing results predicted by the atomistic based continuum (ABC) model developed by Wernik and Meguid [25]. Subsequently, the effect of orientation and agglomeration of CNTs on the bulk elastic properties of the nanocomposite are analysed and discussed.

3.4.1 Comparisons with Existing ABC Results

Recently, Wernik and Meguid [25] developed a novel multiscale ABC approach to determine the elastic properties of CNT-reinforced epoxy composites. In their model, the governing atomistic constitutive laws were integrated within the continuum framework by modeling the CNT as a space-frame-like structure where the adjacent atomic bonds are considered as a load-bearing beam element. Nodes were used to connect the beam elements to form the CNT structure and truss elements were used to represent the vdW interactions at the CNT-polymer interface. After obtaining the elastic properties of the representative fiber, comprising a CNT, the surrounding epoxy and their interface, they calculated the bulk elastic properties of the nanocomposite using large-scale hybrid Monte Carlo finite element simulations. The concept of the representative fiber is similar to that of the nanocomposite RVE used in the current study. Thus, to validate the present multiscale model, the results of the developed multiscale model in the current work are compared with those shown in [25] for CNT-reinforced adhesives containing randomly oriented CNTs, as shown in Fig. 3.10.

The results predicted by the present multiscale and the ABC models are in good agreement, validating the multiscale model developed in this study. The difference in the elastic moduli between those provided in Ref. [25] and the current study is attributed to the lower values of $E$ (1.14 GPa) and $G$ (0.41 GPa) of the epoxy used. In our work, the respective elastic moduli $E$ and $G$ for the epoxy were 3.2 GPa and 1.1 GPa. In addition, a uniform distribution of the polymer nodal density (99 nodes/nm$^3$) around the embedded CNT is assumed in Ref. [25], while the polymer nodal density obtained from the MD simulations is found to vary along the radial direction, as shown in Fig. 3.5. At this juncture, it is important to note that the present multiscale model represents the real nanocomposite structure with the minimum assumptions compared to that of the ABC model which model the atomic structure as an equivalent beam and truss.
elements. Thus, it can be inferred from these comparisons that the present multiscale model can be reliably applied to determine the effective elastic properties of nanocomposites.

![Figure 3.10 Comparison of Young’s (E) and shear (G) moduli of the nanocomposite containing randomly oriented CNTs predicted by the present multiscale model with those of ABC model [25].](image)

### 3.4.2 Effect of orientation and agglomeration of CNTs

Unless otherwise stated, the bulk elastic properties of the nanocomposite are relating to the aligned nanocomposite RVEs along the 3-axis. The maximum CNT volume fraction ($V_{\text{CNT}}$) considered in the nanocomposite is 5% because CNT concentrations above this loading are not normally realized [25]. Let us first demonstrate the effect of agglomeration of CNTs on the effective elastic properties of the aligned CNT-reinforced epoxy composite. Considering the epoxy as the matrix phase and the RVE as the reinforcement, the effective elastic coefficients of the nanocomposite were determined by following the micromechanical modeling approach developed in Section 3.2.2. The effective elastic moduli of the nanocomposite are related to the effective elastic stiffness components as follows:

$$E_{33} = C_{33} - \frac{2C_{23}^2}{C_{12} + C_{11}}$$  \hspace{1cm} (3.11)
\[ E_{11} = E_{22} = \frac{(c_{11} - c_{12}) (c_{11}c_{33} + c_{12}c_{33} - 2c_{23}^2)}{c_{11}c_{33} - c_{23}^2} \]  

\[ G_{12} = \frac{(c_{11} - c_{12})}{2} \]  

\[ G_{13} = G_{23} = c_{44} \]  

\[ K_{12} = \frac{c_{11} + c_{12}}{2} \]

where \( E_{33}, E_{11}, G_{23}, G_{12} \) and \( K_{12} \) are the effective axial Young’s, transverse Young’s, axial shear, transverse shear and bulk moduli of the nanocomposite. Figs. 3.11 and 3.12 show the variations of the effective axial Young’s modulus \((E_{33})\) and the transverse Young’s modulus \((E_{11})\) of the nanocomposite against the CNT volume fraction \((V_{CNT})\), respectively.

![Graph](image)

**Figure 3.11** Variation of the effective axial Young’s modulus \((E_{33})\) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

Both moduli exhibit similar trends; with increasing CNT volume fraction, both moduli increase significantly. Significant enhancements are observed in the values of \( E_{33} \) and \( E_{11} \) compared with the pure epoxy matrix, but it is more prominent in the case of the axial Young’s modulus \((E_{33})\). It may also be observed that the effect of agglomeration of CNTs on these constants becomes more pronounced at higher CNT volume fraction \((> 2\%)\). At 5 vol% of CNTs, the nanocomposite
containing bundles of three and seven CNTs, the values of $E_{33}$ are decreased by $\sim 20\%$ and $\sim 37\%$ as compared with the nanocomposite reinforced with individual CNTs, respectively. For the same CNT loading, the percentage reductions in the values of $E_{33}$ of the nanocomposite containing bundles of three and seven CNTs are found to be $\sim 12\%$ and $\sim 23\%$ in comparison to the nanocomposite reinforced with individual CNTs, respectively. Figs. 3.13 and 3.14 show the variations of the effective axial shear modulus ($G_{23}$) and the transverse shear modulus ($G_{12}$) of the nanocomposite with the CNT volume fraction, respectively.

![Graph](image)

**Figure 3.12** Variation of the effective transverse Young’s modulus ($E_{11}$) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

The CNT bundling (agglomeration) significantly reduced the effective axial shear modulus of the composites from 2.55 to 1.7 GPa (i.e., around $\sim 33\%$ reduction in case of bundle of three CNTs) and from 2.55 to 1.4 GPa (i.e., around $\sim 45\%$ reduction in case of bundle of seven CNTs), at 5 vol\% of CNTs. On the other hand, the agglomeration of three CNTs has a marginal effect on the transverse shear modulus ($G_{12}$) while agglomeration of seven CNTs has significant effect on the same and decreases its value up to 26%, at 5 vol\% of CNTs. Figure 3.15 demonstrate that the CNT bundling has marginal effect on the effective bulk moduli ($K_{12}$) of the nanocomposite.
**Figure 3.13** Variation of the effective axial shear modulus ($G_{23}$) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

**Figure 3.14** Variation of the effective transverse shear modulus ($G_{12}$) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.
Figure 3.15 Variation of the effective bulk modulus ($K_{12}$) of the aligned CNT-reinforced epoxy composite with the CNT volume fraction.

It is worth noting that the results predicted by our multiscale model as depicted in Figs. 3.11–3.15 show clearly that the agglomeration of CNTs significantly affects the elastic moduli and has a marginal influence on the bulk modulus of the nanocomposite. This happens because the interfacial properties of the nanocomposites deteriorate with increasing bundle size. The presence of the bundle leads to a reduction of the interface area between the CNTs and the matrix (see Fig. 3.8).

In the previous set of results (Figs. 3.11–3.15), the effect of agglomeration of CNTs on the effective properties of the aligned CNT-reinforced epoxy composite is studied. Practically, the orientations of the CNT reinforcement in the polymer matrix can vary over the volume of the synthesized nanocomposite. Therefore, studying the properties of nanocomposites reinforced with randomly oriented CNTs is of a great importance. For such investigation, CNTs or their bundles are considered to be randomly dispersed in the epoxy matrix over the volume of the nanocomposite. As expected, this case provides the isotropic elastic properties for the resulting nanocomposite.
Figure 3.16 Variation of the effective Young’s modulus ($E$) of the nanocomposite containing randomly oriented CNTs with the CNT volume fraction.

Figure 3.17 Variation of the effective shear modulus ($G$) of the nanocomposite containing randomly oriented CNTs with the CNT volume fraction.

Figs. 3.16 and 3.17 illustrate the variations of the effective Young’s ($E$) and shear ($G$) moduli of the nanocomposite with the CNT loading, respectively. These results clearly demonstrate that the randomly dispersed CNTs improve the effective Young’s and shear moduli of the nanocomposite.
over those of the transverse Young’s modulus ($E_{11}$) and the shear moduli ($G_{12}$ and $G_{23}$) of the nanocomposite reinforced with aligned CNTs. This is attributed to the fact that the CNTs are homogeneously dispersed in the epoxy matrix in the random case and hence the overall elastic properties of the resulting nanocomposite improve in comparison to the aligned case. These findings are also consistent with the previously reported findings [22, 25]. It may also be observed that both $E$ and $G$ decrease with the increase in the number of CNTs in the bundle, and this effect becomes more pronounced at higher volume fractions of CNTs.

### 3.5 Conclusions

In this article, we develop a multiscale model to determine the bulk elastic properties of CNT-reinforced epoxy composites. Two aspects of the work were examined. First, MD simulations were carried out to determine the transversely isotropic properties of nanocomposite RVEs containing either an individual CNT or CNT bundles embedded in an epoxy matrix. The isotropic elastic properties of the pure epoxy were also obtained from the MD simulations. Second, the developed RVEs were, in turn, used with analytical micromechanical technique of the Mori-Tanaka type to determine the bulk elastic properties of the nanocomposite. This model was then validated by comparing the predicted results with those of a hybrid atomistic-based continuum model. The developed model was applied to investigate the influence of the orientation and agglomeration of the dispersed CNTs on the elastic properties of CNT-epoxy composites. The following is a summary of our findings:

1. The presence of CNT agglomerates in the nanocomposite degrades its effective elastic properties,
2. The effective elastic properties of the nanocomposites decrease with the increase of the CNT agglomerate size,
3. Randomly oriented CNTs or their bundles have significant influence on the elastic properties of the nanocomposite considered,
4. The transverse Young’s modulus, the axial shear and the transverse shear moduli of nanocomposites reinforced with aligned CNTs are less than those of the randomly dispersed case, and
5. The multiscale model developed in this study is capable of determining the effective elastic properties of any advanced nanocomposite containing either aligned or randomly dispersed CNTs.

### 3.6 Acknowledgements

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### 3.7 References

37 http://nanoengineer-1.software.informer.com/.
Chapter 4.
Paper #2: Multiscale modeling of the effect of waviness and agglomeration of CNTs on the elastic properties of nanocomposites

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4.1 Abstract

In this paper, a multiscale model, based on MD simulations and micromechanics (MM) modeling techniques, was developed to determine the effect of waviness and agglomeration of CNTs on the elastic bulk properties of nanoreinforced polymer composites. This effort extends our earlier work which examines the effects of volume fraction, orientation, and agglomeration of straight CNTs on the effective elastic properties of polymer nanocomposites. The predictions of our earlier studies provided an overestimate of the examined elastic properties of the considered polymer nanocomposite. We believe this difference is due mainly to the unrealistic assumption that CNTs are straight reinforcements, which is contrary to the experimental findings. Unfortunately, most existing multiscale models assume straight CNTs. In this extension, we overcame this limitation by using more realistic wavy CNTs. RVEs reinforced with either single or bundles of wavy CNTs were developed to study the effect of waviness, agglomeration, and orientation of CNTs on the bulk properties of the nanocomposite considered. A shape factor \( \alpha \) was introduced to represent the degree of curvature of wavy CNTs. In this case, CNTs of sinusoidal shapes with different curvatures ranging from straight \( (\alpha=0) \) to severely curved \( (\alpha=1.67) \) nanotubes were modeled. Unlike our earlier study, where the reinforced polymer composite was assumed to be transversely isotropic, in this work - due to waviness of CNTs - the reinforced polymer is treated as orthotropic. The results show that CNT waviness limits the reinforcement effects of the embedded nanotubes. However, the effect of waviness diminishes and stabilizes after a certain shape factor value \( \alpha \). The predictions of the current multiscale model are in very good agreement with the experimental
findings of earlier studies, verifying its validity and reliability. It can be concluded from the current study that waviness and agglomeration are key parameters that dictate the elastic properties of CNT-reinforced polymer composites.

4.2 Introduction

Owing to their remarkable mechanical and physical properties, it is believed that few weight percentages of CNTs can significantly improve the mechanical, electrical, and thermal properties of CNT-based composites [1-3]. Such composites have found its way into different -industrial applications such as electrostatic-assisted painting and electromagnetic interference shielding in automotive and aerospace industries, load-bearing applications in sporting goods industry and enhanced fiber composites in wind turbine blades and security boats [4]. More advanced applications that require multifunctional materials are being explored including structural health monitoring and lightning-strike protection for aerospace vehicles [4,5].

A significant number of experimental, numerical, and theoretical studies have been conducted to investigate the potential use of CNTs as reinforcing fibers [6,7]. Meguid and Sun [8] studied experimentally the tensile debonding of epoxy reinforced with homogeneously dispersed CNTs. Their results showed an improvement in the mechanical properties only at lower CNT concentrations as at higher weight fractions the dispersed CNTs tend to agglomerate and aggregate. Allaoui et al. [9] significantly enhanced the mechanical properties of MWCNT–epoxy composites with 200% increase in Young’s modulus over the pure epoxy with only 1 wt% of nanotubes. Li et al. [10] managed to prepare CNT–reinforced epoxy composites with relatively higher weight fractions of CNTs and significant improvement in the properties. Their results showed that at 5 wt% of CNTs, Young’s modulus increased from 4 to 7 GPa. The achieved improvement in the mechanical properties of CNT reinforced polymer composites is bounded by many factors such as uniform distribution, agglomeration, waviness of the nanotubes and the strength of the interface between the embedded nanotubes and the surrounding matrix. To study the influence of those parameters on the overall behavior of nanocomposites, several multiscale models have also been developed [11]. In general, multiscale modeling of nanocomposites can be achieved in two consecutive steps. At the nanoscale level, molecular dynamics (MD) simulation [12] or atomistic based continuum (ABC) technique [13] can be used to obtain the effective elastic
properties of a representative volume element (RVE) consisting of a CNT embedded in an epoxy matrix. At the bulk level, micromechanical models or finite element (FE) simulations can then be used to scale up these nanoscale properties to the microscale leading to the bulk properties of the composite [6,7,11].

Despite the remarkable elastic properties of CNTs, the reported experimental results in the literature show a limited enhancement in the effective elastic properties of their nanocomposites compared to the numerical and theoretical predictions [6,11,14]. The limited enhancement in the properties is attributed to different parameters such as agglomeration and aggregation of CNTs, poor interfacial properties, CNT waviness, quality of CNTs (i.e. purities, geometry and aspect ratios), and CNT orientation [11-16]. The presence of agglomerates limits the reinforcement effect of the strong individual CNTs and leads to a nanocomposite with inferior properties when compared with the pure matrix [18]. This can be attributed to the rapid decrease in the strength of the nanotube bundle with the increase of its diameter due to the slippage of the nanotubes within the bundle. This slippage limits the stress transfer between the nanotubes inside the bundle and between the nanotubes and the surrounding polymer matrix [18]. The dispersed CNTs in the synthesized composite usually have some curvature due to their extremely high aspect ratio and very low bending stiffness [17]. Due to their high flexibility, CNTs tend to bend or unfold when dispersed in polymer matrices, as shown in Fig. 4.1 [11,14,19]. The processing of such nanocomposites usually includes a mixing step that uses both mechanical steering and sonication processes to homogenously disperse nanotubes and breaks up any agglomerates in the prepared composites [1]. Due to the induced curvature, the elastic moduli of the nanotubes and consequently the nanocomposite will vary significantly in all directions [14]. For example, the reinforcing effect will increase in the transverse direction and decrease in the chord direction with increasing CNT curvature.

Several experimental and theoretical studies have been conducted to investigate the effects of the agglomeration and waviness on the mechanical properties of CNT-polypropylene composites [16-22]. The average size of the CNT agglomerates was measured using atomic force microscopy and were found to be ~200 nm, while the diameter of the individual MWCNTs was ~25 nm [20]. The presence of the agglomerates limited the stress transfer between the nanotubes and the polymer and led to composites with reduced elastic moduli [20]. Shi et al. [21] were among the first group
to theoretically study the effect of waviness and agglomeration on the elastic properties of CNT-polymer composites using micromechanics. The effective properties of nanocomposites reinforced with either helical nanotube or spherical agglomerates were obtained. Their results showed that both waviness and agglomeration degrade the bulk properties of the nanocomposite significantly. Weidt et al. [22] developed a 3D finite element model to predict the compressive behavior of epoxy matrix reinforced with curved nanotubes. The properties of the nanotubes and the CNT-polymer interface were determined using molecular dynamics simulations. The waviness of CNTs was found to reduce the elastic modulus and the yield strength of the nanocomposite. On the other hand, Nafar et al. [16] found that wavy CNTs enhance the effective stiffness properties of the nanocomposite using a micromechanical model for weak bonded CNTs.

![Experimental results showing wavy nature of CNTs](image)

**Figure 4.1** Experimental results showing wavy nature of CNTs: (a) SEM image of CNT-epoxy composites with different scales and (b) A schematic representation of agglomerated and wavy CNTS (After [19]).

We believe that considering CNT waviness and agglomeration in multiscale modeling is very crucial for predicting the actual elastic properties of nanocomposite materials [11,14]. Previous models that considered CNT-polymer composites reinforced with isolated well dispersed straight CNTs predicted mechanical properties that are much higher than the experimental measurements. To overcome this problem, many researchers developed micromechanical and FE models that consider wavy and agglomerated nanotubes. However, most of these models considered perfect bonding between the matrix and the reinforcing fibers and neglected the discrete nature of the nanocomposites at the nanoscale level. CNTs were consistently assumed in these models as solid cylinders with isotropic or transversely isotropic properties [11,14] with limited consideration to the size effect.
From the above literature review, it can be concluded that a reliable model that considers these imperfections at the atomic level is highly desirable as it will overcome these inherent and artificially imposed limitations. To the best of the authors' knowledge, they are unaware of a comparable study. The present study is intended to fill this gap in the literature. It considers a multiscale model, based on molecular dynamics simulations and micromechanical modeling techniques, to study the effect of nanotube waviness and agglomeration on the elastic properties of CNT-polymer nanocomposites. First, MD simulations of a wavy CNT embedded in an epoxy matrix will be conducted to determine the effective elastic moduli at the nanoscale. Then, Mori-Tanaka micromechanical technique will be used to scale up these properties to the microscale level and to determine the effect of CNT waviness and orientation on the bulk properties. The obtained numerical results will be validated with recently obtained experimental findings.

### 4.3 Multiscale modeling

In order to design nanocomposites properly and optimize their properties, the effect of all variables, including nanotube waviness and agglomeration, on their performance must be considered. Controlling such parameters experimentally can be quite difficult and intricate. Therefore, a reliable multiscale model that accounts for all imperfections is highly desirable. In this study, a new multiscale model based on MD simulations and micromechanical modeling is developed in two steps to determine the effects of CNT waviness and agglomeration on the effective elastic properties CNT-reinforced composites. The bulk properties of the nanocomposite are obtained in two consecutive steps. First, MD simulations are used to determine the stiffness tensors of the neat epoxy and the epoxy matrix reinforced with CNTs. CNTs with different curvatures were assumed as reinforcement fibers, while the agglomeration effect is captured by considering nanotube bundles of different diameters. Second, Mori-Tanka micromechanical technique is used to scale up the obtained properties and to study the effect of nanotube agglomeration, waviness, and orientation on the bulk properties of the material. Fig. 4.2 shows the steps involved in the hierarchical multiscale model. The proposed multiscale model will consider only weak bonding (van der Waal and electrostatic forces) between nanotubes and matrix that represent unfunctionalized CNTs.
In the present study, MD simulations are used to determine the effective elastic properties of the nanocomposite constituents at the nanoscale. MD simulations offer an appropriate and effective means to deal with large systems and relatively longer simulation times compared to density functional theory simulations. All MD simulations were conducted with large-scale atomic/molecular massively parallel simulator (LAMMPS) [23] using the consistent valence force field (CVFF) [24]. This force field has been successfully used to predict the elastic properties of CNTs and epoxy polymers [12,25-28]. All interactions between the CNT and the polymer molecules are nonbonded interactions that originate from the van der Waals (vdW) interactions and electrostatic forces. The cut-off distance for these interactions is set to 14.0 Å [29]. Periodic boundary conditions are imposed on all directions of the RVE [30]. The atomic structure and properties of the neat epoxy are taken from our earlier paper [12].

### 4.4.1 Modeling of nanocomposite reinforced with wavy CNTs

Due to the relatively high aspect ratio of CNTs and their low bending stiffness, they tend to bend forming wavy and curved nanotubes in the manufactured nanocomposites (see Fig. 4.3(a)). MD simulations will be conducted for RVEs reinforced with wavy nanotubes of different curvatures, as shown in Fig. 4.3(b). In the proposed model, nanotubes are considered to have a sinusoidal shape:
\[ y = a \cos \left( \frac{\pi z}{2\lambda} \right) \quad \text{with} \quad z \in [0, \lambda] \quad (4.1) \]

where \(a\) and \(\lambda\) are the amplitude and the quarter wavelength of the wavy nanotube, respectively [32]. The parameter \(\alpha = a/\lambda\) is used as a shape parameter that defines the degree of curvature of the nanotube. Due to symmetry and the applied periodic boundary and loading conditions, only half of a complete sine-curved nanotube is considered in the MD simulations [33]. Seven curved single wall carbon nanotubes were generated and equilibrated before using them as reinforcement fibers in the RVE of the nanocomposites. All nanotubes are (5,5) armchair SWCNT of length 256 Å. The aspect ratio (Length/diameter) of the modeled nanotubes is \(\sim 400\), which is relatively high compared with earlier MD simulations reported in [28,34]. The simulation region in each case was constructed by randomly placing the cross-linked epoxy structures around the embedded nanotube, as shown in Fig. 4.4. The size of the RVE in each case was adjusted in such a way that the CNT volume fraction in it remains constant at 1.8%. The details of the seven RVEs are summarized in Table 4.1.

**Table 4.1** Parameters used in the RVEs with wavy (5,5) SWCNTs of length 256 Å at \(\sim 1.8\) vol %.

<table>
<thead>
<tr>
<th>Case #</th>
<th>(\lambda) (Å)</th>
<th>(\lambda) (Å)</th>
<th>Shape Parameter ((\alpha = a/\lambda))</th>
<th>No of DGEBA Resins</th>
<th>No of TETA Curing agents</th>
<th>Total No. of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>127.9</td>
<td>0.0</td>
<td></td>
<td></td>
<td>2050</td>
</tr>
<tr>
<td>2</td>
<td>33.7</td>
<td>121.1</td>
<td>0.28</td>
<td></td>
<td></td>
<td>1025</td>
</tr>
<tr>
<td>3</td>
<td>58.8</td>
<td>108.6</td>
<td>0.54</td>
<td></td>
<td></td>
<td>1.34×10⁵</td>
</tr>
<tr>
<td>4</td>
<td>73.9</td>
<td>96.1</td>
<td>0.77</td>
<td></td>
<td></td>
<td>2050</td>
</tr>
<tr>
<td>5</td>
<td>84.6</td>
<td>83.6</td>
<td>1.01</td>
<td></td>
<td></td>
<td>1025</td>
</tr>
<tr>
<td>6</td>
<td>92.2</td>
<td>71.1</td>
<td>1.28</td>
<td></td>
<td></td>
<td>1.34×10⁵</td>
</tr>
<tr>
<td>7</td>
<td>97.7</td>
<td>58.6</td>
<td>1.67</td>
<td></td>
<td></td>
<td>2050</td>
</tr>
</tbody>
</table>

**Table 4.2** Details of the simulated RVEs with agglomerated wavy SWCNTs.

<table>
<thead>
<tr>
<th>Case #</th>
<th>No of CNTs</th>
<th>Shape Parameter ((\alpha = a/\lambda))</th>
<th>No of DGEBA resins</th>
<th>No of TETA Curing agents</th>
<th>Total number of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.54</td>
<td>907</td>
<td>454</td>
<td>0.60×10⁴</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.54</td>
<td>2300</td>
<td>1150</td>
<td>1.50×10⁵</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.54</td>
<td>6470</td>
<td>3230</td>
<td>4.29×10⁵</td>
</tr>
</tbody>
</table>
CNTs tend to agglomerate and aggregate into bundles due to their high surface energy and surface area [35]. As a result, the reinforcement effects of the nanotubes decrease dramatically in nanotailored composites. The combined influence of CNT waviness and agglomeration on the bulk elastic properties of CNT-based composites is examined here by considering RVEs reinforced with either individual or agglomerated bundles of wavy CNTs. For such an investigation, three RVEs are constructed to represent an epoxy matrix containing: (i) a single
CNT, (ii) a bundle of three CNTs, and (iii) a bundle of seven CNTs (see Figs. 4.5 and 4.6). The initial distance between the adjacent CNTs in each bundle was taken to be 3.4 Å, which is the intertube separation distance in multi-walled CNTs [36]. In order to highlight the joint effect of agglomeration and waviness, we selected a moderately curved CNTs with a shape parameter $\alpha=0.54$. The size of the RVE in each case was adjusted in such a way that the CNT volume fraction in it remains constant at ~4.0%. The details of the three RVEs are summarized in Table 4.2.

Figure 4.5 CNT bundle consists of seven CNTs used in the MD simulations to represent agglomerated nanotubes.

Figure 4.6 CNT bundle consists of three CNTs used in the MD simulations to represent agglomerated nanotubes.
4.4.3 Boundary Conditions

Curved nanotubes have reinforcement effects on both the chord and the transverse directions. Therefore, in order to determine the properties of nanocomposites reinforced with wavy CNTs, the RVEs are assumed to be orthotropic. Therefore, nine independent material constants are required to fully define the elastic stiffness matrix of the RVE. The constitutive relationship of the orthotropic RVE is given by

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix} \begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{bmatrix}
\]

(4.2)

where \(\sigma_{ij}\) and \(\varepsilon_{ij}\) are the respective stress and strain components and \(C_{ij}\) represents the elastic coefficients of the RVE. The corresponding elastic constants can be explicitly determined using the following relations:

\[
E_i = \left( C_{11}C_{22}C_{33} + 2C_{23}C_{12}C_{13} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 \right) / \left( C_{22}C_{33} - C_{23}^2 \right)
\]

\[
E_2 = \left( C_{11}C_{22}C_{33} + 2C_{23}C_{12}C_{13} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 \right) / \left( C_{11}C_{33} - C_{13}^2 \right)
\]

\[
E_3 = \left( C_{11}C_{22}C_{33} + 2C_{23}C_{12}C_{13} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 \right) / \left( C_{11}C_{22} - C_{12}^2 \right)
\]

\[
\nu_{21} = \left( C_{12}C_{33} - C_{13}C_{23} \right) \left/ \left( C_{11}C_{33} - C_{13}^2 \right) \right., \quad \nu_{21} = \left( C_{12}C_{33} - C_{13}C_{23} \right) \left/ \left( C_{11}C_{33} - C_{13}^2 \right) \right.
\]

\[
\nu_{31} = \left( C_{13}C_{22} - C_{12}C_{23} \right) \left/ \left( C_{11}C_{22} - C_{12}^2 \right) \right., \quad \nu_{31} = \left( C_{13}C_{22} - C_{12}C_{23} \right) \left/ \left( C_{11}C_{22} - C_{12}^2 \right) \right.
\]

\[
\nu_{23} = \left( C_{11}C_{23} - C_{12}C_{13} \right) \left/ \left( C_{11}C_{33} - C_{13}^2 \right) \right., \quad \nu_{32} = \left( C_{11}C_{23} - C_{12}C_{13} \right) \left/ \left( C_{11}C_{22} - C_{12}^2 \right) \right.
\]

\[
\mu_{23} = C_{44}, \quad \mu_{13} = C_{55}, \quad \mu_{12} = C_{66}
\]

where \(E_i\), \(\nu_{ij}\), and \(\mu_{ij}\) with \((i, j = 1, 2, 3)\) are Young’s modulus, Poisson's ratio, and shear modulus, respectively [37]. In order to determine the stiffness coefficients, each RVE is subjected to the following tests: uniaxial tension and compressions in all directions, and in-plane shear in 1-2, 2-3, and 1-3 planes, as shown in Fig. 4.7.
Figure 4.7 Schematic representations of the applied loading conditions and the predicted elastic constants for the different loading cases.

4.4.4 Molecular Dynamics Implementation

A series of MD simulations have been carried out to determine the elastic moduli of the RVEs using the constant-strain energy minimization method. Predefined deformations were applied on the MD unit cell and the obtained viral stress tensor was then used to determine its effective stiffness constants. The applied strain in each loading case and the corresponding stiffness constants are summarized and listed in Table 4.3. After each strain increment, the MD unit cell is equilibrated in the NVT ensemble at 300 K for 10 ps. Then, the induced stresses are averaged over an interval of 10 ps to reduce the effect of fluctuations. These previous steps were repeated again in the subsequent strain increments until the total strain reached up to 2.5%.

4.4.5 Micromechanical Modeling

The obtained stiffness tensors of the RVEs from the MD simulations accurately capture the mechanical behavior of the nanocomposite at the nanoscale level and represent the bridge to the microscale level. These RVEs are used in the micromechanical modeling as an effective fiber, while the pure epoxy is used as the surrounding matrix that is perfectly bonded with these fibers [39,40]. Different analytical and numerical techniques have been developed over the last decade.
to determine the bulk behavior of CNT reinforced composites and to predict their effective properties. Wernik and Meguid [13] used large scale FE analysis and Mori-Tanaka micromechanical model to determine the effective properties of CNT-epoxy composites. Their results show a good agreement between the two methods, indicating the validity and reliability of the Mori-Tanaka method for the current study. Mori-Tanaka method assumes that each inclusion is embedded in an infinite medium subjected to an effective stress or an effective strain in the far field, allowing the average stress field and overall effective stiffness to be determined [12,13]. The details of the Mori–Tanaka solution for a two-phase composite are not presented here but can be found in our earlier publication [12].

### Table 4-3 Effective elastic coefficients of the RVEs and the corresponding displacement fields.

<table>
<thead>
<tr>
<th>Elastic coefficients</th>
<th>Applied strains</th>
<th>Applied displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}, C_{12}, C_{13}$</td>
<td>$\varepsilon_{11} = e$</td>
<td>$u_1 = ex_1$</td>
</tr>
<tr>
<td>$C_{22}, C_{12}, C_{13}$</td>
<td>$\varepsilon_{22} = e$</td>
<td>$u_2 = ex_2$</td>
</tr>
<tr>
<td>$C_{33}, C_{13}, C_{23}$</td>
<td>$\varepsilon_{33} = e$</td>
<td>$u_3 = ex_3$</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>$\varepsilon_{23} = e/2$</td>
<td>$u_2 = \frac{e}{2}x_3$, $u_3 = \frac{e}{2}x_2$</td>
</tr>
<tr>
<td>$C_{55}$</td>
<td>$\varepsilon_{13} = e/2$</td>
<td>$u_1 = \frac{e}{2}x_2$, $u_3 = \frac{e}{2}x_3$</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>$\varepsilon_{12} = e/2$</td>
<td>$u_1 = \frac{e}{2}x_2$, $u_2 = \frac{e}{2}x_1$</td>
</tr>
</tbody>
</table>

### 4.5 Results and Discussion

In this Section, the results of the MD simulations are first presented for RVEs reinforced with individual wavy CNT or agglomerated CNT bundles of different sizes. Subsequently, the effect of waviness, agglomeration and orientation of CNTs on the bulk elastic properties of CNT-epoxy nanocomposites are analysed and discussed. The results of the developed multiscale model are compared with the reported experimental results for similar nanocomposites [41].

#### 4.5.1 MD Results and Nanoscale Level Properties

A series of MD simulations were carried out to determine the orthotropic stiffness tensor of RVEs reinforced with either an individual CNT or bundles of CNTs. The effects of nanotube waviness
on the nanoscale properties of the nanocomposite were studied by changing the waviness parameter, α, from 0 to 1.67, to represent a wide range of curvatures. Seven RVEs reinforced with wavy nanotubes at ~2.0 vol % were modeled and nine stiffness constants were determined from the stress strain curves for each RVE. Table 4.4 summarizes the outcome of the MD simulations for wavy cases.

<table>
<thead>
<tr>
<th>Waviness Parameter (α)</th>
<th>C_{11} (GPa)</th>
<th>C_{22} (GPa)</th>
<th>C_{33} (GPa)</th>
<th>C_{12} (GPa)</th>
<th>C_{13} (GPa)</th>
<th>C_{23} (GPa)</th>
<th>C_{44} (GPa)</th>
<th>C_{55} (GPa)</th>
<th>C_{66} (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7.0</td>
<td>7.0</td>
<td>30.16</td>
<td>5.48</td>
<td>5.62</td>
<td>6.74</td>
<td>1.44</td>
<td>1.44</td>
<td>1.67</td>
</tr>
<tr>
<td>0.28</td>
<td>7.1</td>
<td>7.7</td>
<td>22.72</td>
<td>6.99</td>
<td>5.02</td>
<td>5.32</td>
<td>1.41</td>
<td>1.44</td>
<td>2.27</td>
</tr>
<tr>
<td>0.54</td>
<td>6.9</td>
<td>7.9</td>
<td>17.81</td>
<td>5.99</td>
<td>4.65</td>
<td>5.17</td>
<td>1.50</td>
<td>1.47</td>
<td>1.90</td>
</tr>
<tr>
<td>0.77</td>
<td>7.5</td>
<td>8.5</td>
<td>14.34</td>
<td>6.145</td>
<td>5.07</td>
<td>5.44</td>
<td>1.22</td>
<td>1.60</td>
<td>.165</td>
</tr>
<tr>
<td>1.01</td>
<td>7.4</td>
<td>8.8</td>
<td>13.21</td>
<td>6.515</td>
<td>5.13</td>
<td>5.48</td>
<td>1.42</td>
<td>1.50</td>
<td>2.14</td>
</tr>
<tr>
<td>1.28</td>
<td>7.2</td>
<td>9.3</td>
<td>12.23</td>
<td>5.82</td>
<td>4.98</td>
<td>5.40</td>
<td>1.22</td>
<td>1.27</td>
<td>1.73</td>
</tr>
<tr>
<td>1.67</td>
<td>7.0</td>
<td>10.1</td>
<td>11.32</td>
<td>5.77</td>
<td>4.93</td>
<td>5.17</td>
<td>1.56</td>
<td>1.42</td>
<td>1.78</td>
</tr>
</tbody>
</table>

The properties of the pure epoxy were taken from our previous study [12]. In this investigation, the same epoxy structure was studied and the predicted Young’s modulus and Poisson’s ratio were 3.175 GPa and 0.39, respectively. It may be observed from the results that the elastic properties of the RVEs are significantly higher than those of the neat epoxy. It is also clear that the CNT waviness reduces the reinforcing effect of the embedded CNTs, which eventually degrades the bulk elastic moduli of the nanocomposites. The stiffness constant C_{33} along the longitudinal direction of the straight CNT (α=0.0) lost two third of its maximum value when compared with the severely curved CNT (α=1.67). On the other hand, the stiffness component C_{22} along the transverse direction increased by increasing the curvature, indicating an improvement in the reinforcement effect in the lateral direction compared with the straight nanotubes. For example, the C_{22} increased from 7 MPa for the RVE reinforced with straight (α=0.0) CNT to 10.1 MPa for the RVE reinforced with curved CNT (α=1.67). The shear moduli of the RVEs showed slight improvement over the pure epoxy and their values fluctuate with the magnitude of the waviness
factor $\alpha$. It is worth noting that each RVE will be used as an effective fiber in the micromechanical model to calculate the influence of waviness of CNTs on the bulk elastic moduli of CNT-epoxy composites (see Fig. 4.1).

In our previous study, we examined the effect of agglomeration on the elastic properties of CNT-epoxy composites [12]. In the current, we examine the combined effect of agglomeration and waviness by considering nanotube bundles of wavy CNTs. Three RVEs reinforced with single CNT, bundle of three CNTs, and bundle of seven CNTs were modeled, respectively. As we covered a wide range of nanotube curvatures from straight ($\alpha=0$) to severely curved ($\alpha=1.67$), the CNTs in the agglomeration study were all wavy with a moderate waviness parameter $\alpha = 0.54$ and volume fraction $\approx 2.0\%$. This value of curvature was selected to represent a realistic composite microstructure that contains agglomerated CNTs with an averaged wavy structure. The predicted stiffness constants from the MD simulations are summarized in Table 4.5. It may be observed from the results that the CNT agglomeration reduces the reinforcing effect of the CNTs leading to nanocomposites with reduced bulk properties. Almost all the elastic constants decreased significantly by increasing the size of CNT bundle. For instance, the longitudinal elastic coefficients ($C_{33}$) of the RVEs reinforced with bundles of three and seven CNTs decreased by 12.6% and 23.9%, respectively, as compared with the RVE containing an individual CNT. This deterioration of the properties is attributed to the weak interaction between the nanotube’s bundle, which limits the load transfer inside the bundle, and consequently from the epoxy to the embedded nanotubes. As the size of the bundle increases, the interface area with the surrounding polymer decreases and these growing agglomerates start to act as stress concentrators rather than reinforcement fibers. These values of the elastic moduli show the combined effect of the agglomeration and waviness in reducing the elastic constants of the nanocomposite compared with those reinforced with well-dispersed straight CNTs. Again, each RVE will be used as an effective fiber in the micromechanical model to calculate the influence of agglomeration and waviness on the bulk elastic moduli of CNT-epoxy composites (see Fig. 4.1).
Table 4-5 Effective elastic coefficients of the RVEs reinforced with agglomerated wavy CNTs at 3.5 vol %. The waviness parameter, $\alpha$, of the CNTs is 0.54.

<table>
<thead>
<tr>
<th>No of CNTs</th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{23}$</th>
<th>$C_{44}$</th>
<th>$C_{55}$</th>
<th>$C_{66}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>14.0</td>
<td>15.5</td>
<td>23.0</td>
<td>11.1</td>
<td>8.5</td>
<td>8.2</td>
<td>1.21</td>
<td>1.75</td>
<td>1.6</td>
</tr>
<tr>
<td>Three</td>
<td>12.4</td>
<td>13.0</td>
<td>20.1</td>
<td>10.7</td>
<td>98.1</td>
<td>7.4</td>
<td>1.15</td>
<td>1.54</td>
<td>1.34</td>
</tr>
<tr>
<td>Seven</td>
<td>10.1</td>
<td>10.5</td>
<td>17.5</td>
<td>9.4</td>
<td>7.5</td>
<td>7.2</td>
<td>1.1</td>
<td>1.32</td>
<td>1.12</td>
</tr>
</tbody>
</table>

4.5.2 Micromechanics Results and Bulk Properties

The predicted nanoscale elastic moduli of the RVEs are used as input to the microscale level analysis to predict the effective bulk properties of the nanocomposites. In our work, the respective elastic moduli $E$ and $G$ for the epoxy were 3.175 GPa and 1.14 GPa [12]. Considering the pure epoxy as the matrix phase and the RVEs as the reinforcement fibers, Mori-Tanka micromechanical method was used to study the effect of nanotube waviness, agglomeration, and orientation on the effective properties of CNT-epoxy composites.

Effect of waviness

The reported results in the scientific literature indicates that the overall enhancement of the elastic properties as measured experimentally is much lower than the theoretical predications [41,42]. CNT waviness is considered, among other parameters, as a key factor in determining the performance of the composite. Figure 4.8(a) and (b) show the predicted variation of Young’s modulus $E$ and shear modulus $G$ of nanocomposites reinforced with randomly oriented wavy nanotubes with the CNT volume fraction. It is very clear that effective elastic moduli of the nanocomposite reduce significantly with increasing the curvature of the nanotubes. However, the effect of waviness stable after $\alpha=0.75$, as shown in Fig. 4.9. This fluctuation of the bulk elastic moduli around its minimum value at $\alpha=0.75$ can be attributed to the reduction of the longitudinal elastic modulus and simultaneous increase in the transverse elastic constant of the effective fiber after reaching this curvature. At 2.0 vol % of CNTs, Young’s and shear moduli decreased by $\sim36\%$ with increasing the nanotube curvature ($\alpha$) from 0 to 1.67. This one third loss in the elastic moduli indicates the significant role of the waviness on the overall performance of the considered nanocomposite. The results predicted by the present multiscale model are compared with the
experimental results for CNT-epoxy composites examined in Ref. [41]. The figures show a good agreement between the reported experimental results and nanocomposites reinforced using wavy CNTs, validating the multiscale model developed in this study and indicating the importance of considering nanotube waviness in any future model.

**Figure 4.8** Effect of CNT waviness on the bulk elastic moduli of CNT/epoxy composites (all nanotubes are well dispersed).
Combined effect of waviness and agglomeration

The agglomeration of CNTs limits their reinforcement effect. This is because it reduces the stress transfer from the matrix to the embedded nanotubes, resulting in a composite with deteriorated properties over the neat polymer [12]. The combined effect of CNT waviness and agglomeration is considered by modeling RVEs reinforced with bundles of wavy CNTs. All CNTs have a sinusoidal shape with a shape factor (\( \alpha \)) equal 0.54. The respective effective elastic constants of three RVEs reinforced with a single CNT, a bundle of three CNTs, and a bundle of seven CNTs were determined using MD simulations. These properties are then scaled up to the bulk level using Mori-Tanaka method to study the effect of agglomeration on the effective properties of the considered nanocomposite. All the results mentioned in this section are for randomly distributed nanotubes leading to isotropic nanocomposite. The effect of orientation will be covered in the next section. Figs. 4.10(a) and (b) show the variations of the effective Young’s modulus \( E \) and shear modulus \( G \) of the nanocomposite with the CNT loading for the three agglomeration cases, the well-dispersed straight case, and the experimental results for a similar nanocomposite system from the literature.
The results indicate that the CNT agglomeration has a significant effect on the bulk elastic properties of the nanocomposite and this effect increases with the increase in the number of CNTs in the bundle (see Fig. 4.11). It may also be observed that the effect of agglomeration of CNTs on these constants becomes more pronounced at higher CNT volume fraction (>2%). For example,

Figure 4.10 Effect of CNT agglomeration on the bulk elastic moduli of CNT/epoxy composites (all nanotubes are wavy with curvature parameter $\alpha=0.54$).
Young’s and shear moduli of the nanocomposites reinforced with bundles of three and seven CNTs decreased by ~18% and ~39%, respectively, as compared with nanocomposite reinforced with individual wavy CNTs. Fig. 4.10(a) shows that at 3.5 vol % of CNTs, the effective Young’s modulus of the composite reduced from ~13 GPa for the straight individual CNTs case to ~8 GPa for the wavy individual CNTs case to ~5 GPa for the agglomerated wavy CNTs case. This reduction on the effective properties of the composite because of CNT agglomeration and waviness shows their crucial effect on the bulk properties of their nanocomposites [12,13]. The experimental results of Young’s modulus agree with the determined properties for the agglomerated cases from the developed multi-scale model.

![Graph showing the variation of Young’s modulus and shear modulus with the number of nanotube on the CNT bundle.](image)

**Figure 4.11** The variation of Young’s modulus and shear modulus with the number of nanotube on the CNT bundle.

**Effect of Orientation**

The orientations of the CNTs in the produced composite can vary from totally randomly oriented to perfectly aligned [43,44]. As a result, the effective elastic properties of the produced nanocomposite will largely depend on the orientation of the reinforcing CNTs. Therefore, to study this parameter, nanocomposites reinforced with either randomly oriented or perfectly aligned CNTs are considered. All CNTs are wavy with a shape factor $\alpha=0.54$ and only well dispersed (i.e. individual) nanotubes are presented in the current orientation investigation. The predicted bulk stiffness tensor of the nanocomposite from the micromechanical analysis for the randomly
oriented case is isotropic, while the aligned case is orthotropic. Fig. 4.12(a) illustrate the variations of the effective Young’s modulus ($E$) for the randomly oriented case and the effective axial ($E_{33}$), transverse ($E_{11}$), and shear ($G$) moduli for the aligned case with the CNT loading. The variation of the effective shear modulus for the randomly oriented and the in-plane shear modulus for the aligned cases with the CNT loading is shown in Fig. 4.12(b).

**Figure 4.12** Effect of CNT orientation on bulk elastic moduli of CNT/epoxy composites (all nanotubes are wavy with shape parameter $\alpha=0.54$).
The results indicate that the introduced alignment of CNTs only improves the effective elastic moduli along the alignment direction while reducing the effective transverse elastic and shear moduli of the nanocomposite, as compared with the nanocomposite reinforced with randomly oriented CNTs. For example, at 3.5 vol % of CNTs, Young’s modulus increased from 8.2 GPa for the random CNT case to 17.5 GPa along the alignment direction for the aligned CNT case. Along the transverse direction, this alignment reduced the elastic constant less significantly to 5.6 GPa. The shear moduli ($G_{12}$) was also reduced due to the alignment from 3.0 GPa for the randomly oriented CNTs to 1.6 GPa. The nanocomposite reinforced with aligned CNTs. These findings are also consistent with the previous studies [45].

### 4.6 Conclusions

In this article, we developed a multiscale model to determine the effect of nanotube waviness, agglomeration and orientation on the bulk elastic moduli of CNT-reinforced epoxy composites. MD simulations were performed to determine the orthotropic stiffness tensor of RVEs containing epoxy matrix reinforced with either an individual nanotube or CNT bundles. The effect of waviness was considered by modeling wavy nanotube with different curvatures, ranging from straight to severely curved. The obtained properties from the MD simulations were then used as an input to the micromechanical model to determine the effect of waviness, agglomeration, and orientation of CNTs on the bulk elastic properties of the nanocomposite. The proposed model was then validated by comparing the predicted results with the experimental results for similar nanocomposite system [41]. These modeling procedures include minimum assumptions compared to previous models and are able to represent the real nanocomposite structures [12,28]. Thus, the present multiscale model can be reliably applied to determine the bulk properties of any advanced nanocomposite. The following is a summary of our findings:

1. The effective elastic properties of the nanocomposite decrease significantly with increasing the waviness of the embedded CNTs, and stabilize after reaching their minimum values at a certain CNT shape factor $\alpha$,

2. The effective elastic properties of the nanocomposite decrease significantly with the presence of CNT agglomerates due to the weak stress transfer inside the nanotube bundles
and from these bundles to the surrounding matrix. In addition, these properties also decrease with the increase of the CNT agglomerate size,

3. The combined effect of agglomeration and waviness results in a significant reduction in the bulk properties of the nanocomposite,

4. The alignment of CNTs improves the effective axial Young’s modulus of the nanocomposite along the alignment direction and reduces the transverse Young’s and shear moduli of the nanocomposite, and

5. The predicted elastic properties are in a good agreement with the reported experimental results.

4.7 Acknowledgements

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4.8 References

19 J. Wernik, PhD, University of Toronto, 2013.
Chapter 5.
Paper #3: Large-Scale Atomistic Simulations of CNT-Reinforced Thermoplastic Polymers

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5.1 Abstract

Different multiscale techniques were developed over the past two decades for modeling CNT-reinforced composites. However, these techniques contained numerous approximations to allow scaling up the properties from nanoscale to bulk levels. These approximations were partly responsible for the anomaly between model predictions and experiments. In this study, we overcame this problem by modeling large (up to one million atoms) representative volume elements (RVEs) reinforced by CNTs with different lengths (aspect ratio up to 500), curvatures (ranging from straight to severely curved) and bundle sizes to simulate actual nanocomposites. The RVE dimensions were carefully selected to ensure that the molecular structure of the nanocomposite is successfully represented and the obtained elastic properties are independent of the RVE size. A series of extensive MD simulations were conducted to determine the elastic moduli of the nanocomposite using the constant-strain energy minimization method. The developed models were verified by comparing their predictions with the reported experimental results. The developed MD models were further used to study the effect of CNT morphology and the state of dispersion on the elastic moduli of CNT-polyethylene composite. The current model can be integrated with electrical and thermal models to predict the multifunctional properties of CNT-reinforced composites.

Keywords: Molecular dynamics, Nanocomposites, Elastic properties, Carbon nanotube morphology, Agglomeration, Waviness.
5.2 Introduction

CNTs are considered to be an ideal reinforcement for polymers [1–5] because of their outstanding mechanical properties, low density, high aspect ratio, and exceptionally high surface area to weight ratio [1,6]. Understanding the nanocomposite behavior and the associated reinforcement mechanism at the atomic level is very critical in utilizing this new material at the industrial level [2,5,7]. However, due to the enormous computational cost required for atomistic modeling of large scale systems representing CNT-reinforced composites and the inherent technical difficulties in preparing and testing their multifunctional properties, several analytical and numerical techniques were developed to model these advanced materials [4,8–10]. Furthermore, different multiscale modeling schemes were proposed to bridge the atomic structure of the nanocomposite at the nanoscale level and the bulk behavior of the material at the macroscale level [11–15]. These techniques were used by several research groups to investigate the reinforcement mechanism of CNTs in polymers and to evaluate the impact of the following parameters on the mechanical properties: dispersion state, agglomeration, alignment, morphology, and chemical functionalization [16].

Interestingly, despite the extraordinary properties of SWCNTs, the reported enhancement in the mechanical properties of their polymer composites [17,18] is significantly lower than what analytical and numerical studies have predicted [19,20]. The main reason for the contradicting results is the inability of these modeling techniques to represent the actual microstructure of the nanocomposites as imaged by electron microscopy [21]. For example, Eshelby’s equivalent inclusion assumes a perfect bonding between the reinforcing CNTs and the surrounding polymer matrix. This assumption contradicts the atomic nature of CNT-reinforced composites at the nanoscale level where the adhesion between the composite constituents is mostly caused by weak nonbonded interactions such as van der Waals forces [4,22]. Several attempts have been made to overcome this problem, for example, Mohammadi et al. [23] developed a three-phase multiscale technique to model the debonding between the embedded CNTs and the surrounding matrix using the cohesive zone method. Savvas et al. [24] used SEM images to create a stochastic description of the morphology and distribution of the CNTs inside the nanocomposite. The embedded element technique was then used in their finite element (FE) simulations to obtain the mechanical properties of the equivalent RVEs. Furthermore, in order to model the atomic structure of the
nanocomposite, the Coarse-grained (CG) modeling technique was used to model CNT-reinforced composites by several research groups [12,25,26]. In the CG method, both polymer monomer and CNT atomic rings are grouped into strings of beads that are connected with Hookean springs [12,27]. This mapping mechanism reduces the computation cost significantly and hence increases the size of the RVEs and the timescale of the simulations [26].

Molecular dynamics have been used to guide experimental design of nanocomposites by providing fundamental insights into the reinforcement mechanism and the nature of the filler–matrix interface [1,4,28]. Several attempts have been recently made to study CNT-reinforced composites directly using MD simulations of RVEs reinforced with a large number of randomly dispersed [1,5,29] or aligned [30] CNTs. For example, Zhang et al. [1] studied the effect of temperature on the mechanical performance of SWCNT/epoxy composites using MD simulations of RVEs reinforced with randomly dispersed short CNTs. Furthermore, the effect of chemical functionalization on the elastic and fracture properties of Acrylate polymer reinforced with CNTs was evaluated using reactive MD simulation by Jensen et al. [31] In their study, they determined the elastic moduli, yield strength, and fracture strength of RVEs compromised from CNTs and the matrix polymer. More recently, Khare et al. [29] conducted comprehensive MD simulations of RVEs reinforced with either well dispersed or agglomerated short CNTs to study the influence of agglomeration on the glass transition behavior of CNT-epoxy composites. Despite these attempts to model CNT-reinforced composites using MD simulations, several assumptions and limitations were considered in previous studies eventually leading to either under estimating the properties because of considering only extremely short CNTs to reduce the computation cost [1,5,29] or overestimation of the material performance by assuming all CNTs to be perfectly aligned and infinitely long (assuming periodic boundary condition along the nanotubes axis) [30]. We believe that these atomistic based studies failed to truly represent the actual microstructure of the nanocomposite.

Unlike previous investigations, for evaluating the mechanical properties of CNT-reinforced composites at the microscale level, we directly modeled the actual microstructure of the nanocomposite as indicated by SEM and AFM images using large scale MD simulations. CNTs with different lengths, curvatures and bundle sizes were used to model the actual morphology of the composite. The properties of the nanocomposite were obtained by averaging the results of
enough number of RVEs. Different parameters were investigated separately in this paper to obtain their impact on the mechanical properties, namely, RVE size, CNT agglomeration, CNT morphology, and CNT concentration. This work was achievable due to the use of a supercomputer (SHARCNET) to model relatively large MD systems (i.e. number of atoms up to \( \sim 9 \times 10^5 \) atoms) compared to previous studies. The constructed RVEs allowed us to incorporate enough number of CNTs that have large aspect ratios up to 450. The obtained results from our atomistic simulations were compared to those obtained experimentally in the literature and a through discussion of the reinforcement mechanism of the embedded CNTs was presented.

### 5.3 Modeling Strategy

To this end, significant progress has been made in modeling and characterization CNT-reinforced composites, and numerous studies have been conducted to study the effect of dispersion state and morphology of CNTs on the mechanical and interfacial properties [4]. However, none of the previous atomistic studies were able to model the actual microstructure of the nanocomposite, as determined by SEM and AFM imaging studies. Here, we present a comprehensive investigation of the elastic properties of CNT-reinforced composites through MD simulations of large RVEs that make use of realistic shapes on CNTs as determined experimentally using our SEM and AFM measurements, as shown in Fig. 5.1.

Modeling of such large atomic systems enabled us to model realistic nanostructure reinforced with long CNTs in contrast to previous studies that only considered small systems reinforced with unrealistically short CNTs to reduce the computational burden. To the best of our knowledge, this is the first time that MD simulations conducted for atomic systems large enough to represent realistic nanocomposites systems. Furthermore, the effects of system size (i.e. number of CNTs at the same volume fraction), CNT agglomeration, CNT volume fraction, and CNT morphology on the elastic properties have been considered in this study. The influence of CNT morphology was considered by modeling CNTs with different curvatures starting from straight to severely curved, while the effect of agglomeration was captured by considering CNT bundles consisting of three and seven nanotubes, as shown in Fig. 5.1(c). Polyethylene (PE) polymer of short chain-length was used as the matrix material. This simple polymer allowed us to focus more on constructing the reinforcing CNTs and building the complex RVEs. Additionally, in order to
reduce the effect of CNTs distribution inside the RVE on the predicted properties, two RVEs were generated for each case study and the elastic moduli were obtained by averaging the moduli obtained from three MD simulations of each RVE (uniaxial loading in x, y, and z directions).

Figure 5.1 Steps involved in the multiscale model: (a) an image of a CNT-reinforced composite sample, (b) an AFM image of the nanocomposite, (c) a RVE mimicking the composite microstructure with varied shapes and bundles of CNTs used as reinforcements.

5.3.1 Modeling of Reinforcing CNTs

Agglomeration and waviness of the dispersed CNTs inside the matrix reduce their reinforcement effect. This is due to the dramatic reduction in load transfer between the matrix and the CNTs [32,33]. Figure 5.2 shows a SEM image of as-received CNTs and how they were modeled in this study. CNTs tend to agglomerate and aggregate into bundles due to their high surface energy and
surface area, as shown in Fig. 5.2. They self-organize into bundles in the shape of hexagonal-packing arrangements [33] with sizes ranging from several to hundreds of CNTs [34]. In this study, two bundles consisting of three and seven CNTs were created to evaluate the effect of agglomerate size on the elastic properties, as shown in Fig. 5.1(c). The initial distance between neighboring CNTs in each bundle was set to 3.4 Å (i.e. equivalent to the intertube separation distance in MWCNTs) [35]. CNTs also become curved upon dispersion in the polymer matrix due to their extremely high aspect ratio and flexibility, as shown in Fig. 5.2 [19,36]. As a result of the induced deformation and curvature in the structure of the dispersed CNTs, the elastic stiffness of the CNTs and consequently the composite will vary significantly in all directions [36]. The waviness effect on the elastic properties of CNT-reinforced composites was addressed in this study by considering two sinusoidally shaped CNTs as reinforcements in the RVEs (see Fig. 5.1(c)) [21]. These two wavy CNTs were selected to represent a wide range of CNTs curvatures, as seen by the conducted AFM and SEM image analysis†, as shown in Fig. 5.1(b) and Fig. 5.2(a). The parameter $\alpha=a/\lambda$ is introduced to define the curvature severity of the CNT (with $\alpha=0$ for a straight CNT and $\alpha>0$ for a curved CNT), where $\lambda$ and $a$ are the wavelength and the amplitude of the CNT, respectively. The effect of CNT aspect ratio was also investigated by considering three CNTs of different lengths, as shown in Fig. 5.1(c). All CNTs were generated and equilibrated before dispersing them in the RVEs. The structural details (chirality, length, waviness, bundle size) of all CNTs used in this study as reinforcements are summarized in Table 5.1.

Table 5-1 Parameters of the SWCNTs used in the MD simulations. All CNTs are armchair with (5,5) chirality and 6.78 Å diameter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CNT # 1</th>
<th>CNT # 2</th>
<th>CNT # 3</th>
<th>CNT # 4</th>
<th>CNT # 5</th>
<th>CNT # 6</th>
<th>CNT # 7</th>
</tr>
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<tbody>
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<td>305</td>
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<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>7</td>
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<td>2200</td>
<td>2470</td>
<td>3300</td>
<td>7700</td>
</tr>
</tbody>
</table>

† A detailed description of the experimental measurement of the morphology and dispersion state are provided in Appendix 3.
Figure 5.2 (a) Morphology and distribution state of as-received CNTs from a microstructure image measured with SEM, schematic representations of (b) two bundles of three and seven CNTs, and (c) a wavy CNT in the shape of a sine wave.

5.3.2 Modeling of CNT-Reinforced PE Composite

The modeling procedure of the RVEs was as follows: (i) constructing of the reinforcing CNTs, (ii) constructing the polymer chains, and (iii) packing the composite constituents randomly inside the simulation cell. Polyethylene was selected as the matrix material for our MD simulations and to establish the baseline properties of the matrix prior to the inclusion of CNTs. The details of the selection and the modeling procedures of the neat PE are discussed and presented in our previous paper [37]. Selecting the MD unit cell dimensions is very critical in limiting the required computational cost for our simulations. On the other hand, the dimensions of the atomistic system must be large enough to eliminate the boundary and size effects due to the limited number of CNTs used as reinforcement fibers in smaller RVEs. We investigated the effect of system size by comparing the results for four RVEs of different sizes and reinforced with 2.0 vol.% of CNTs. We introduce a new parameter called the size ratio of the unit cell, SRRVE, which is equal to the ratio between the side length of the cube and the length of the longest embedded CNT. Figure 5.3 shows the smallest and largest systems that were used in our size effect study; the left is the smallest system with SRRVE = 0.83, which means that the three embedded CNTs were not allowed to align along any direction, and the right is the largest system with SRRVE = 1.51 and reinforced by 18 CNTs. The details of the constructed RVEs are summarized in Table 5.2.
Figure 5.3 RVEs with (a) SRRVE = 0.83 and reinforced with 3 CNTs, and (b) SRRVE = 1.51 and reinforced with 18 CNTs. All PE chains are omitted from this figure for graphical purposes and all CNTs are SWCNTs with chirality (5,5) and AR=200. The CNT volume fraction in all RVEs is 2.0%.

Table 5-2 Details of the RVEs used in investigating the system size effect on the elastic properties of CNT-PE composite. All CNTs are armchair with (5,5) chirality, 131.0 Å length, and 6.78 Å diameter. The CNT volume fraction in all RVEs is 2.0%.

<table>
<thead>
<tr>
<th>Case #</th>
<th>SRRVE</th>
<th>System dimensions</th>
<th>No. of CNTs</th>
<th>No of PE chains</th>
<th>Total No. of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.83</td>
<td>110.5</td>
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<td>2132</td>
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<td>2</td>
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<td>8466</td>
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<td>4</td>
<td>1.51</td>
<td>200.5</td>
<td>18</td>
<td>12733</td>
<td>809,225</td>
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</tbody>
</table>

5.3.3 Development of RVEs with different CNT volume fractions

We constructed RVEs with increasing CNT concentrations up to 5 vol.% to study the effect of CNT volume fraction on the elastic properties of CNT-PE composite. All CNTs used in this investigation are SWCNT of (5,5) chirality with aspect ratio 100. All CNTs were placed randomly inside RVEs representing a homogeneous nanocomposite with isotropic properties. Fig. 5.4(a)-(c) show RVEs reinforced with 1.0 vol.%, 3.0 vol.%, and 5.0 vol.% of CNTs, respectively. We limited our simulations to RVEs with volume fraction up to 5% because at higher CNT concentrations, the elastic properties of the nanocomposite were found to deteriorate due to the
aggregation and agglomeration of CNTs inside the manufactured composite [7]. For each volume fraction, two RVEs were generated to represent different nanotubes arrangements inside the MD unit cell. The details of the six RVEs examined are summarized in Table 5.3.

![Image](image.png)

**Figure 5.4** RVEs reinforced with (a) 1.0 vol.% (b) 3.0 vol.%, and (c) 5.0 vol.% of CNTs. All PE chains are omitted from this figure for graphical purposes and all CNTs are SWCNTs with chirality (5,5) and aspect ratio of 100.

**Table 5-3** Details of the RVEs used in investigating the CNT volume fraction impact on the elastic properties. All CNTs are armchair with (5,5) chirality, 68.0 Å length, AR = 100, and 6.78 Å diameter. The side length of all RVEs is 122.5 Å.

<table>
<thead>
<tr>
<th>Case #</th>
<th>CNT vol.%</th>
<th>No. of CNTs</th>
<th>No of PE chains</th>
<th>Total No. of atoms</th>
</tr>
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<td>5.0</td>
<td>20</td>
<td>2850</td>
<td>187900</td>
</tr>
</tbody>
</table>

**5.3.4 Development of RVEs with different CNTs bundle sizes**

Three different nanocomposite systems were created and simulated in the agglomeration study, as shown in Fig. 5.5. The size of the RVE was adjusted in all cases to keep the CNT volume fraction constant at 3.0%. In the first RVE, 35 CNTs were randomly placed inside the cube to represent a composite with well-dispersed CNTs (see Fig. 5.5(a)). The properties obtained from this system will be used as a reference for comparison with the other two cases representing agglomerated CNTs. Two agglomeration cases were considered in this analysis: 5 bundles with each consisting
of three CNTs were dispersed randomly inside the RVE (see Fig. 5.5(b)), and 2 bundles with each consisting of seven CNTs were also dispersed randomly inside the RVE (see Fig. 5.5(c)). For each considered case, two RVEs were generated to represent different nanotubes arrangements inside the MD unit cell. The details of the three RVEs examined are summarized in Table 5.4.

![Figure 5.5 RVEs reinforced with (a) 26 well dispersed CNTs, (b) 5 bundles with each consisting of three CNTs, and (c) 2 bundles with each consisting of seven CNTs. The PE chains are omitted from this figure for graphical purposes.](image)

**Table 5-4** Details of the RVEs used in investigating the CNT agglomeration impact on the elastic properties. All CNTs are armchair with (5,5) chirality, 131.0 Å length, AR = 200, and 6.78 Å diameter. The CNT volume fraction in all RVEs is 3.0%.

<table>
<thead>
<tr>
<th>Case #</th>
<th>MD cell size (Å)</th>
<th>No of CNT/reinforcement</th>
<th>No. of reinforcements</th>
<th>No of PE chains</th>
<th>Total No. of atoms</th>
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</thead>
<tbody>
<tr>
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<td>2</td>
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</tr>
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<td>1</td>
<td>14</td>
<td>6551</td>
<td>421,586</td>
</tr>
</tbody>
</table>

**5.3.5 Development of RVEs with different CNT morphologies**

One of the major limitations of existing micromechanical models is their inability to model the actual morphology of nanocomposites, as seen in AFM and SEM images. To overcome this problem, three RVEs (see Fig. 5.6) were created to model PE polymer reinforced by 3.0 vol.% of CNTs with different morphologies. Figure 5.6(a) shows a RVE representing a realistic nanocomposite morphology, where CNTs of different length, curvatures, and bundle sizes were dispersed randomly inside the MD unit cell. Figure 5.6(b) shows a RVE representing idealized
nanocomposite reinforced with well-dispersed straight CNTs. Figure 5.6(c) shows a RVE reinforced with bundles of CNTs, each bundle is constructed from 7 CNTs. The details of all RVEs are summarized in Table 5.5.

**Table 5-5** Details of the RVEs used in the effect CNT morphology study. All CNTs are SWCNTs with chirality (5,5) and they represent 3.0 vol.% in total.

<table>
<thead>
<tr>
<th>Case #</th>
<th>RVE side length (Å)</th>
<th>No. of CNTs/bundles</th>
<th>CNT per bundle</th>
<th>Aspect ratio</th>
<th>No of PE chains</th>
<th>Total No. of atoms</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>7</td>
<td>200</td>
<td></td>
<td>12942</td>
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<td>3</td>
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<td></td>
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<td>202</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>12942</td>
<td>832100</td>
</tr>
<tr>
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<td>202</td>
<td>1</td>
<td>1</td>
<td>150</td>
<td></td>
<td></td>
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<td>1</td>
<td>207</td>
<td>12942</td>
<td>852054</td>
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<td>4</td>
<td>7</td>
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<td>13332</td>
<td>857362</td>
</tr>
</tbody>
</table>

### 5.4 MD simulations

We conducted extensive MD simulations to determine the elastic properties of CNT-reinforced PE composite using the constant-strain energy minimization method. The PE polymer, the reinforcing CNTs, and the interactions between the matrix and the CNTs were modeled and simulated with the LAMMPS [38] software using the AIREBO potential [39]. A detailed description of the interatomic potential and the parameters (cut-off distance, boundary conditions) used in our simulations is presented in our previous papers [21,37]. The reinforcing CNTs were dispersed randomly inside the constructed RVEs. Therefore, all RVEs were considered to be isotropic and hence only two elastic constants were required to fully define the stiffness tensor of the nanocomposite system. The constitutive relationship of the isotropic RVE is given by
\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{bmatrix} =
\begin{bmatrix}
C_{11}^* & C_{12}^* & C_{12}^* & 0 & 0 & 0 \\
C_{12}^* & C_{11}^* & C_{12}^* & 0 & 0 & 0 \\
C_{12}^* & C_{12}^* & C_{11}^* & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{2}(C_{11}^* - C_{12}^*) & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2}(C_{11}^* - C_{12}^*) & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{2}(C_{11}^* - C_{12}^*)
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{bmatrix}
\]

(5.1)

Figure 5.6 RVEs reinforced with (a) 26 well dispersed CNTs of different length, waviness ratios and bundle sizes, (b) 26 well dispersed CNTs, and (c) 4 bundles of CNTs. The PE chains are omitted from this figure for graphical purposes.

where \(\sigma_{ij}\) and \(\varepsilon_{ij}\) are the respective stress and strain components and \(C_{ij}^*\) represents the averaged elastic coefficients of the RVE. For isotropic materials, \(C_{11} = C_{22} = C_{33}\), \(C_{12} = C_{13} = C_{23}\), and \(C_{44} = C_{55} = C_{66}\); however, due to the limited size of the RVE and the relatively small number of reinforcing CNTs compared to actual nanocomposites, a measurable difference in the obtained properties existed based on the loading direction. To eliminate this anisotropy in the obtained properties, each stiffness component was averaged over the three directions and two RVEs were used for each case study (i.e. each point in the results is the average of six MD simulations). The steps involved in minimizing and equilibrating (adjusting the density, the temperature, and the pressure) the MD systems are presented in our previous paper [11]. In order to determine the stiffness coefficients, each RVE was subjected to a uniaxial compression in \(x\), \(y\), and \(z\)-directions separately (see Table 5.6). During the MD simulations, compression strain increments of 0.25% were sequentially applied along specific coordinate by uniformly compressing the simulation box in this direction and updating the atoms locations to fit within the deformed system. After each
strain increment, the MD unit cell was equilibrated using the NVT ensemble at 300 K for 20 ps and the calculated virial stress tensor was averaged over the last 10 ps of the equilibrium simulation [40]. This loading stage was repeated until reaching a total strain of 2.5%; the nanocomposite systems exhibits a linear stress-strain response over this range. The stiffness coefficients were calculated from the slope of the stress-strain curves and the symmetric components of the stiffness tensor were then averaged from the three MD simulations, as shown in Table 5.6 [11]. Based on the calculated stiffness coefficients, Young’s modulus (E), shear modulus (G) and Poisson’s ratio (ν) were determined by the following relations:

\[
C_{11} = \frac{E(1-\nu)}{(1+\nu)(1-2\nu)}, \quad C_{12} = \frac{E\nu}{(1+\nu)(1-2\nu)}, \quad \text{and} \quad G = \frac{C_{11}-C_{12}}{2}
\]  

(5.2)

<table>
<thead>
<tr>
<th>Applied strains</th>
<th>Applied displacement</th>
<th>Elastic coefficients</th>
<th>Averaged Elastic coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁₁ = e</td>
<td>u₁ = e x₁</td>
<td>C₁₁ = σ₁₁/ε₁₁, C₂₁ = σ₂₂/ε₁₁, C₃₁ = σ₃₃/ε₁₁</td>
<td>C’₁₁ = \frac{C_{11} + C_{22} + C_{33}}{3}</td>
</tr>
<tr>
<td>ε₂₂ = e</td>
<td>u₂ = e x₂</td>
<td>C₁₂ = σ₁₁/ε₂₂, C₂₂ = σ₂₂/ε₂₂, C₃₂ = σ₃₃/ε₂₂</td>
<td>C’₁₂ = \frac{(C_{12} + C_{21} + C_{33} + C_{13} + C_{23} + C_{32})}{6}</td>
</tr>
<tr>
<td>ε₃₃ = e</td>
<td>u₃ = e x₃</td>
<td>C₂₃ = σ₂₃/ε₃₃, C₃₃ = σ₃₃/ε₃₃</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-6 Effective stiffness constants of the RVEs and the corresponding displacement fields.

5.5 Results and discussion

In this section, the effect of the RVE size on the elastic properties of CNT-reinforced composites is first presented and discussed. Subsequently, the effects of CNT’s volume fraction, agglomeration, and morphology on the elastic properties of CNT-PE composites are presented, analyzed and discussed. The results of the conducted large scale atomistic simulations were then compared with the reported experimental and numerical results in the literature [11,41–43].

5.5.1 Effect of RVE size on the elastic properties

In order to obtain a realistic estimation of the mechanical properties of CNT-reinforced composites using MD simulations, the RVE size and hence the number of reinforcing nanotubes must be large enough to truly represent the actual microstructure of the system and to avoid the anisotropy encountered in smaller systems. Four RVEs with increasing sizes representing CNT-PE composites reinforced with the same CNT volume fraction were constructed and modeled to
determine the effect of RVE size on the obtained elastic moduli. Figure 5.7(a) shows the stress-strain curves for RVEs with size ratios \( \frac{L_{cell}}{L_{RVE}} \) ranging from 0.83 to 1.51. Table 5.7 summarizes the stiffness constants and the corresponding elastic moduli obtained from the conducted MD simulations. It is very clear that the system size significantly affects the elastic properties of the composite, indicating its critical role in obtaining reliable results. For example, the RVE with the smallest size \( \text{SR}_{RVE} = 0.83 \) and 135,454 atoms shows a 20.0% increase in Young’s and shear moduli compared to the largest RVE \( \text{SR}_{RVE} = 1.51 \) and 809,225 atoms. Fig. 5.7(b) indicates that Young’s modulus of the composites continued to decrease with increasing the number of the CNTs; the elastic modulus of the system with \( \text{SR}_{RVE} = 1.62 \) is just 1.4% lower than the value obtained for the largest system, indicating a convergence trend. The stiffening seen in the RVE with aspect ratio lower than unity is caused by the inability of the embedded CNTs to align along the x, y, and z-axes (i.e. parallel to the edges of the MD unit cell). CNTs aligned perpendicularly to the loading direction do not contribute as much as the CNTs parallel to the loading direction in resisting the applied deformation. With the increase in the system size, the orientations of the embedded CNTs become more uniformly distributed inside the PE polymer.

**Table 5-7** The stiffness constants and the corresponding elastic moduli determined in the investigation of the effect of RVE size on the mechanical properties of CNT-PE composite. All RVEs are reinforced by 2.0 vol.% of well-dispersed CNTs with AR = 200.

<table>
<thead>
<tr>
<th>( \text{SR}_{RVE} )</th>
<th>Number of CNTs</th>
<th>( C_{11} ) (GPa)</th>
<th>( C_{12} ) (GPa)</th>
<th>( E ) (GPa)</th>
<th>( \nu )</th>
<th>( G ) (GPa)</th>
</tr>
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<tr>
<td>0.83</td>
<td>3</td>
<td>6.45</td>
<td>5.09</td>
<td>1.97</td>
<td>0.44</td>
<td>0.68</td>
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<td>6</td>
<td>5.18</td>
<td>3.96</td>
<td>1.75</td>
<td>0.43</td>
<td>0.61</td>
</tr>
<tr>
<td>1.32</td>
<td>12</td>
<td>4.94</td>
<td>3.83</td>
<td>1.59</td>
<td>0.44</td>
<td>0.55</td>
</tr>
<tr>
<td>1.51</td>
<td>18</td>
<td>5.051</td>
<td>3.93</td>
<td>1.62</td>
<td>0.44</td>
<td>0.56</td>
</tr>
</tbody>
</table>
Figure 5.7 Effect of RVE size: (a) the stress-strain curves obtained from uniaxial compression loading of RVEs with different sizes, and (b) the variation of Young’s modulus and number of atoms with the increase of the system size (the y-axis is normalized by the Young’s modulus of the largest RVE).
5.5.2 Effect of CNT volume fraction on the elastic properties

Existing analytical and numerical investigations have predicted significantly higher elastic properties values when compared with those measured experimentally [44–46]. Here, we report the results of our MD effort concerning the reinforcement effect of randomly dispersed CNTs in a polyethylene matrix with aspect ratios of 100 and volume fractions ranging from 1% to 5%. Figure 5.8(a) shows the stress-strain curves for RVEs with different volume fractions obtained from the numerical uniaxial compression tests ($\varepsilon_x \neq 0$ and $\varepsilon_y = \varepsilon_z = 0$). These curves were used to calculate the stiffness constants along the diagonals ($C_{ii}$ for $i \leq 3$). The variations of the other components of the normal stresses ($\sigma_{22}$ and $\sigma_{33}$) with the applied compression strain ($\varepsilon_x$) were also plotted and their slopes were used to calculate the off-diagonal stiffness components ($C_{ij}$ for $i \neq j$ and $i$ and $j \leq 3$). Table 5.8 summarizes the predicted stiffness constants and the corresponding elastic moduli of the conducted MD simulations for all cases. It is worth noting that each number in that table is the average of three simulations for two different systems. Figure 5.8(b) shows that Young’s modulus of the nanocomposite increases almost linearly with the increase in the CNT volume fraction. The relation between Young’s modulus and the CNT concentration can be described in terms of the following linear function:

$$E = 0.94 + 0.23 \times \text{vol.}\% \text{ (GPa)}$$  \hspace{1cm} (5.3)

Figure 5.8(b) shows a good agreement between the predicted elastic properties obtained from the present MD simulations and the experimental measurements for CNT-PE composites reported in Ref. [42]. This agreement indicates the reliability of the modeling procedures used in our analysis.

<table>
<thead>
<tr>
<th>Vol. %</th>
<th># CNTs</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
<th>$G$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>3.73</td>
<td>3.04</td>
<td>1.01</td>
<td>0.35</td>
<td>0.449</td>
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<td>3.6</td>
<td>1.18</td>
<td>0.41</td>
<td>0.449</td>
</tr>
<tr>
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<td>4</td>
<td>4.65</td>
<td>3.8</td>
<td>1.23</td>
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<td>1.59</td>
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<td>0.442</td>
</tr>
<tr>
<td>4</td>
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<td>4.85</td>
<td>1.94</td>
<td>0.67</td>
<td>0.439</td>
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<tr>
<td>5</td>
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<td>6.35</td>
<td>4.9</td>
<td>2.08</td>
<td>0.73</td>
<td>0.436</td>
</tr>
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</table>

Table 5-8 The stiffness constants and the elastic moduli determined in the investigation of the effect of CNT volume fraction on the mechanical properties of CNT-PE composite. All RVEs of the nanocomposite were reinforced by well-dispersed CNTs with AR = 100.
Figure 5.8 (a) The stress-strain curves obtained from uniaxial compression loading of RVEs reinforced with different CNT volume fractions, and (b) comparison between the obtained elastic properties from our MD simulations and those obtained experimentally by Gorrasi et al. [42]. (The y-axis is normalized by the Young’s modulus of neat polyethylene).
5.5.3 Effect of CNT agglomeration on the elastic properties

The stress-strain curves of the RVEs in terms of the CNT bundle size are depicted in Fig. 5.9(a) for the uniaxial compression MD simulations. The slopes of these curves were used to calculate the stiffness components of the nanocomposite systems. Fig. 5.9(b) shows the variations of Young’s modulus of the nanocomposite with the bundle size. The results indicate that the elastic moduli of the nanocomposite will decrease with the increase in the CNT agglomerate size. The data points in Fig. 5.9(b) were best fitted with the following power law function:

\[ E = 1.6936 \times N_{CNTs}^{-0.1} \text{(GPa)} \]  \hspace{1cm} (5.4)

where NCNTs is the number of CNTs inside the bundle. The decline in the composite properties continued with the increase in the agglomerate size due to the reduction of the exposed surface area of the reinforcing CNTs with the surrounding polymer matrix, which eventually limits the stress transfer between the matrix and the dispersed nanotubes. Interestingly, the elastic modulus of the nanoreinforced composite approaches that of the polymer when the CNT agglomerate diameter approaches ~7 nm (~100 \(d_{CNT}\)). CNT aggregates that have sizes greater than ~100 times the CNT diameter will lead to a composite with lower strength when compared with the pure polymer. Our agglomeration predictions are in very good agreements with the reported results in the literature [11,21,47]. Table 5.9 summarizes the obtained stiffness constants and the corresponding elastic moduli for all cases.

**Table 5.9** The stiffness constants and the corresponding elastic moduli determined in the investigation of the effect of CNT bundle size on the mechanical properties of CNT-PE composite. All RVEs were reinforced by 3.0 vol.% of well-dispersed CNTs with AR = 200.

<table>
<thead>
<tr>
<th>Case #</th>
<th>CNTs/bundle</th>
<th>(C_{11}) (GPa)</th>
<th>(C_{12}) (GPa)</th>
<th>E (GPa)</th>
<th>v</th>
<th>G (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5.9</td>
<td>4.55</td>
<td>1.93</td>
<td>0.436</td>
<td>0.674</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>5.54</td>
<td>4.23</td>
<td>1.88</td>
<td>0.433</td>
<td>0.658</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>5.4</td>
<td>4.25</td>
<td>1.66</td>
<td>0.440</td>
<td>0.576</td>
</tr>
</tbody>
</table>
Figure 5.9 (a) The stress-strain curves obtained from uniaxial compression loading of RVEs with different bundle sizes, and (b) the variation of Young’s modulus with the increase of the CNTs in the bundle.
5.5.4 Effect of CNT morphology on the elastic properties

Three different systems were modeled in this investigation: (i) a RVE reinforced with well-dispersed straight CNTs, (ii) a RVE reinforced by CNTs with different morphologies, and (iii) a RVE reinforced with agglomerated bundle of CNTs. The CNT volume fraction in all RVEs was adjusted to 3% and the systems were cubic of side length ~203 Å. Figure 5.10(a) and (b) show the stress-strain curves obtained for the nanocomposite systems under uniaxial compression loading in the x-direction. The calculated stiffness constants and the elastic moduli for all RVEs are summarized in Table 5.10. It is very clear from the predictions that assuming all CNTs to be straight and well-dispersed in the matrix leads to an overestimation of the composite elastic properties. Additionally, the waviness of CNTs has a smaller impact on the elastic properties of the nanocomposite compared to CNT agglomeration.

Table 5-10 The stiffness constants and the corresponding elastic moduli determined in the investigation of the effect of CNT morphology on the mechanical properties of CNT-PE composite.

<table>
<thead>
<tr>
<th>Case #</th>
<th>C_{11} (GPa)</th>
<th>C_{12} (GPa)</th>
<th>E (GPa)</th>
<th>ν</th>
<th>G (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight CNTs</td>
<td>5.9</td>
<td>4.55</td>
<td>1.93</td>
<td>0.436</td>
<td>0.674</td>
</tr>
<tr>
<td>General morphology</td>
<td>5.54</td>
<td>4.23</td>
<td>1.88</td>
<td>0.433</td>
<td>0.658</td>
</tr>
<tr>
<td>Agglomerated CNTs</td>
<td>5.4</td>
<td>4.25</td>
<td>1.66</td>
<td>0.44</td>
<td>0.576</td>
</tr>
</tbody>
</table>
Figure 5.10 Stress-strain curves for different RVEs considered in the CNT morphology investigation obtained under uniaxial compression loading in the x-direction: (a) the normal stress along the loading direction, and (b) the normal stress perpendicular to the lading direction.

5.6 Conclusions

In summary, we conducted several comparative studies to investigate the effect of CNT concentration, morphology and dispersion state on the elastic properties of CNT-PE composites. The stiffness constants of RVEs reinforced by CNTs with aspect ratios up to 450, waviness ratio ranging from straight to severely curved, and different bundle sizes were determined using the constant-strain energy minimization method. The effect of RVE size and hence the number of CNTs at a specific volume fraction was investigated by modeling RVEs with wide range of dimensions. The following is a summary of our findings:

1. The proper selection of the RVE size is critical in obtaining reliable results as MD unit cells with side length lower than 1.25 the length of the embedded CNTs were found to overestimate the elastic moduli of the nanocomposite by 25%,

2. The adopted large scale atomistic simulations (largest system consists of ~900,000 atoms) are better than current micromechanics techniques such as Mori Tanaka method for modeling nanocomposites with relatively high CNT volume fractions due to the dilute concentration assumption in such analytical solutions [22],
3. The stiffness constants of the nanocomposite increase linearly with the increase of the CNT volume fraction; the magnitude of the elastic modulus almost doubles at a 5 vol.% of CNTs,
4. The presence of CNTs agglomerates significantly limits the reinforcing effect of CNTs and even leads to lowering of the properties when the agglomerate diameter reaches ~100 times the CNT diameter, and
5. Modeling of RVEs reinforced solely by straight CNTs results in overestimation of the elastic properties.

5.7 Acknowledgements

The authors wish to thank NSERC and the Discovery Accelerator Supplement for their kind support of this research.

5.8 References

Chapter 6.
Paper #4: Unraveling the Influence of Grain Boundaries on the Mechanical Behavior of Carbon Nanotubes

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6.1 Abstract

The ability to produce homogeneous defect-free carbon nanotubes (CNTs) represents a major challenge in terms of utility and cost. Specifically, the existence of grain boundaries (GBs) are ubiquitous in large diameter CNTs obtained by various large-scale growth methods and their effects on the mechanical properties of CNTs are not fully explored. Understanding the influence of the grain size and the GB orientation upon the mechanical behavior of CNTs is crucial for their functional and structural applications. The significance and novelty of the current work lies in its ability to establish the mechanical properties and the fracture behaviour of CNTs containing grain boundaries of varied size, orientation and structure to an applied uniaxial load using comprehensive molecular dynamics simulations. A specially developed program, using Voronoi tessellation method and Delaunay triangulation, was implemented to generate the atomistic descriptions of the considered polycrystalline CNTs with a variety of GB morphology. Our results reveal that the mechanical performance of CNTs is significantly affected by the orientations of the GBs, diameter and temperature. In terms of the fracture strength, the resulting failure patterns indicate that the polycrystalline CNTs fail in a brittle fashion and that pentagon-heptagon defects along the GBs serve as crack nucleation sites.

Keywords: Carbon nanotube, Voronoi tessellation, polycrystalline, grain boundaries, mechanical properties, fracture strength
In view of their extraordinary mechanical, thermal, optical, and electronic properties [1, 2], CNTs have attracted intensive interest in many fields such as aerospace, automotive, and bio-nano engineering [3]. While each of these fields exploits a different key property of CNTs, they all implicitly depend on their remarkable mechanical properties for structural reliability and/or sensory characteristics. Due to the inherent limitations of fabrication and purification processes, CNTs typically contain a variety of crystallographic orientations and defects [4]. The common domain interface, grain boundaries (GB), can be regarded as a one-dimensional array of dislocations [5]; some experimental studies also provide evidence of the existence of GBs in CNTs [6-9]. Under certain circumstances, GBs are deliberately introduced for the purpose of tailoring the electronic properties of CNTs to suit the requirements of a particular application. For example, Yao et al. [10] introduced a pentagon and a heptagon into the hexagonal carbon lattice to fuse together two nanotube segments with different atomic and electronic structures to create intramolecular metal-metal, metal-semiconductor, or semiconductor-semiconductor junctions. In another study by Yao et al. [11], well-controlled temperature-mediated growth of intramolecular junctions in CNTs was achieved by changing the temperature during growth. That particular study outlined a potential approach for growing intramolecular junctions in CNTs of different sizes and orientations at desired locations. This is important for tailoring CNT-based electronic circuits. Zhang et al. [12] studied the mechanical properties of 20 representative graphene grains using density functional theory and molecular dynamics (MD). They found that the intrinsic tensile strength of the inflected GBs generally decreases with increasing inflection angle and identified Stone Wales transformation as the major failure mechanism of graphene with GBs at high temperature: whereas the initial fracture site found can be on the boundary line or inside the domain. Electronic properties of polycrystalline CNTs were investigated by Wang et al. [13] using density-functional theory considering parallel and perpendicular GBs to the tube axis. That study reported that the CNTs with parallel GBs have a narrow or zero band gap (<0.16 eV) which is independent of the misorientation angle and the diameter of the CNTs. On the other hand, CNTs with perpendicular GBs show a slightly large band gap (up to 0.6 eV). Zhang et al. [14] carried out MD simulations to determine the mechanical strength and fracture behavior of GBs. Their study revealed that the intrinsic strength, the critical failure strain and the failure mechanism of graphene with GBs mainly rely on the temperature and inflection angle, whereas Young’s
modulus does not vary significantly with temperature or boundary configuration. More recently, quantum transport and thermoelectric properties were reported by Lehmann et al. [5] for graphene sheets, graphene nanoribbons, and CNTs with a variety of GB types in a wide temperature range. Their study demonstrated that GBs are a viable tool to tailor the thermal properties of carbon-based nanomaterials, paving the way for the design of new thermoelectric nano devices. Several studies also reported that by controlling the GBs and creating pores, the band gap in graphene sheets can be tuned, and thus the electronic structure can be controlled via strain engineering [15-17]. The effect of GBs on the mechanical properties of polycrystalline graphene was also investigated using experimental and numerical techniques; see, e.g., Refs. [18-21]. On the contrary, the effects of relatively simple defects such as atom vacancies, doping, substitutional impurities, Thrower-Stone-Wales (TSW) and hybridization, on the thermomechanical properties of CNTs were studied in References [22-24].

Intrinsic topological existence of GBs in polycrystalline CNTs are expected to markedly alter their mechanical properties and failure behavior. It is well-established that the mechanical properties of polycrystalline solids are strongly influenced by their grainy structure. CNTs have been produced in a much controlled environment and as such are less susceptible to large extrinsic defects [25]. Therefore, it is natural to expect the variations in their mechanical properties to arise from intrinsic GBs. These GBs will influence the stress state and may act as a precursor to crack initiation within the CNTs. However, the mechanical properties of CNTs with GBs have not yet been fully explored and investigated. As a result, we lack comprehensive understanding of the influence of these GBs which may limit the remarkable exploitation of the properties of polycrystalline CNTs. Indeed, this has motivated our interest in the current study. Specifically, the focus of our highly original study is to determine the influence of grain size orientation, and atomic structure upon the mechanical properties of polycrystalline CNTs using MD simulations. Additionally, we widen the scope of our research beyond the mechanical properties by investigating the failure behavior and the associated failure mechanisms of polycrystalline CNTs. The outcome of this work should lead to a greater insight into the mechanical behavior and fracture strength of polycrystalline CNTs thus allowing the community to explore the essence of their remarkable multifunctional properties.
6.3 Voronoi tessellation and polycrystalline CNTs

In this work, we created polycrystalline CNTs by rolling graphene sheets containing GBs. The atomic structures of the graphene sheets with randomly distributed grain sizes and shapes were created by using Voronoi tessellation technique [26, 27]. First, based on the required average grain size, a specific number of points were randomly placed inside a square. Second, Delaunay triangulation was performed to obtain a set of spatial coordinates that forms a minimum distance with each nucleus from the randomly created grain nuclei. The circumcenter of neighbouring triangles that was generated in the last step was connected to create GBs and form a particular grain for each nucleus in our simulation cell. Although the grain nuclei were placed randomly, the distribution of the grain sizes (grain area) can be fitted following a gamma distribution [28]. This method has been widely used to model the grain structures in polycrystalline graphene sheets [29, 30]. Figure 6.1 demonstrates three typical grain size distributions in polycrystalline graphene sheets generated from the Voronoi construction. Figure 6.2 shows the systematic steps involved in creating the graphene sheet with randomly distributed GBs, which was then rolled to create a polycrystalline CNT. We generated a collection of polygons separated by planar cell walls perpendicular to lines connecting neighbouring nucleation sites, as shown in Fig. 6.2(a). A polycrystalline graphene sheet was constructed by filling each cell with randomly oriented graphene domains, where the atoms adjacent to the planar cell walls represent the GBs. The initial C–C bond length in the graphene sheets was set to 1.41 Å, which has been confirmed experimentally [3]. Several polycrystalline graphene sheets with dimensions of 30 nm × 30 nm and an average grain size ranging from 5 nm to 10 nm were constructed (see Fig. 6.2(b)). Several regions at different locations inside the polycrystalline graphene with dimensions of 80 Å × 80 Å were selected and extracted to create the basic structure that is rolled to form CNTs, as shown in Fig. 6.2(c). Pentagons and heptagons were created at the boundaries of the grains in each extracted region and then the energy of a graphene system was minimized using the conjugate gradient method to obtain its optimized structure (see Fig. 6.3). The obtained structure was then annealed by equilibrating it at room temperature in the constant temperature and volume canonical (NVT) ensemble over 100 ps with 0.5 fs time step using the velocity Verlet algorithm. The annealing process allows the rearrangement of C–C atomic positions at the GBs [31]. The annealed structures were further equilibrated using the isothermal–isobaric (NPT) ensemble over another 100 ps at 300 K and 1 atm to reach the atmospheric pressure.
In polycrystalline graphene, the GBs have 1D interface between two domains of a material with different crystallographic orientations. The structure of the grain is defined by its orientation angle $\theta_i$, where $\theta_i$ is the angle between the zigzag direction (n,0) and the horizontal axis (see Fig. 6.3). We can also define the tilt angle $\varphi_i$ of a GB as the joint between two mismatched angles ($\theta_L$ and $\theta_R$) of adjacent grains, as shown in Fig. 6.3.

Accordingly, the chiral vectors for the left ($n_L$, $m_L$) and the right ($n_R$, $m_R$) grains along the GB can be defined as follows [15]:

\[
\sin(\theta) = \frac{\sqrt{3} m}{2\sqrt{n^2 + nm + m^2}}, \quad \text{and} \quad (6.1)
\]
\[
\cos(\theta) = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}} \quad (6.2)
\]

These equations can be bridged to obtain the tilt angle ($\varphi$), such that [32]:

\[
\varphi = \tan^{-1} \left[ \frac{\sqrt{3}m_L}{m_L + 2n_L} \right] + \tan^{-1} \left[ \frac{\sqrt{3}m_R}{m_R + 2n_R} \right] \quad (6.3)
\]
Figure 6.2 (a) A plot of a 600 Å × 600 Å square region filled with randomly distributed grains with different sizes and shapes created using Voronoi tessellation technique. The square at the center shows the part of the system filled with randomly oriented graphene domains to create the tessellated graphene sheet. (b) Snapshot of an unequilibrated polycrystalline graphene sheet of a size 300 Å × 300 Å. The square at the bottom edge shows the part of the graphene system that is rolled to form a polycrystalline CNT. (c) An enlarged view of the graphene sheet with 4 grains. Angles of the corresponding crystallographic direction of the grains are determined with respect to the horizontal axis (see Table 6.1 for details). (d) and (e) procedures used to create the polycrystalline CNT.
In principle, different arrangements can develop along the GB. Formation of pentagon and heptagon defects along the GB can develop and defects such as quadrilaterals, octagons, and nonagons can also form due to higher formation energy, and are rarely observed in experiments [33]. Therefore, we consider pentagon and heptagon defects in this work and ruled out all other types of defects. These kinds of GB structures in graphene have also been modeled in several studies [18, 21, 34, 35]. To study the effect of grain shape, size and structure on the mechanical properties of polycrystalline CNTs, four types of CNTs were considered, (see Fig. 6.4). These are: CNT with (i) random GBs, (ii) helical GBs to the CNT axis, (iii) parallel GB to the CNT axis, and (iv) transverse GB to the CNT axis. Grains are shown in different colors and shapes.

Note that the misorientation angle ($\phi$) of a GB can take any value due to a variety of synthesis of CNTs. In case of graphene, the GBs obtained through MD simulations via rotation and reflection operations followed by the annealing process exhibited misorientation angles from $5^0$ to $30^0$ [36], which is in good agreement with the experimental findings reported in [37]. Such misorientation angles of GBs may influence the mechanical properties of CNTs. For each selected polycrystalline CNT, we performed simulations of three randomly generated samples with the same average grain size, but different initial grain configurations, and then used the average of the three samples to determine the averaged mechanical properties. In Table 6.1, we summarized the grain numbers and orientation angles from our simulations. Additionally, the effects of diameter and curvature of CNTs on their mechanical properties and the thermodynamic stability
of the GBs were studied herein by modeling three polycrystalline CNTs with horizontal GB of different diameters ranging from 9 Å to 24 Å, as depicted in Fig. 6.5.

![Image](image_url)

**Figure 6.4** Different cases of polycrystalline CNTs: (a) CNT with random GBs. (b) CNT with helical GBs. (c) Parallel GB to the CNT axis. (d) Transverse GB to the CNT axis.

**Table 6-1** Orientation of grains in polycrystalline CNTs.

<table>
<thead>
<tr>
<th>Type of GBs</th>
<th>Grain number</th>
<th>Sample 1, $\theta_1$ (°)</th>
<th>Sample 2, $\theta_1$ (°)</th>
<th>Sample 3, $\theta_1$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random GBs</td>
<td>1</td>
<td>5.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>26.6</td>
<td>10.5</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>18.7</td>
<td>23.0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>24.5</td>
<td>42.7</td>
<td>45.6</td>
</tr>
<tr>
<td>Helical GB</td>
<td>1</td>
<td>6.4</td>
<td>1.8</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.4</td>
<td>22.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Parallel GB</td>
<td>1</td>
<td>5.6</td>
<td>17.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>27.6</td>
<td>14.7</td>
<td>12.9</td>
</tr>
<tr>
<td>Transverse GB</td>
<td>1</td>
<td>5.6</td>
<td>17.3</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>27.6</td>
<td>14.7</td>
<td>12.9</td>
</tr>
</tbody>
</table>
Figure 6.5 Atomic structures of CNTs with a horizontal GB and different diameters.

6.4 Molecular dynamics (MD) simulations

All MD simulation runs were conducted with large-scale atomic/molecular massively parallel simulator (LAMMPS) [38] and the molecular interactions in CNTs are described in terms of Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) force fields [39]. This interatomic potential accurately captures the interaction between carbon atoms as well as bond breaking and reforming [40, 41]. The cutoff parameter describing the short-range C-C interaction was selected to be 2.0 Å in order to avoid spuriously high bond forces and nonphysical results at large deformation [42, 43]. The interlayer separation distance between graphite layers, 3.4 Å, was taken as the effective thickness of the CNT [22, 44-48].

The sequence of the conducted MD simulations is as follows. First, the initial structures of the CNTs were created by rolling the graphene sheets. The grains of the rolled CNT were then heated up to 3000 K and equilibrated for 100 ps in the NVT ensemble to enable the formation of the pentagon-heptagon rings along the GBs. The obtained structure was then analyzed and the regions with high atomic density that failed to yield a perfect geometry were reconstructed by removing few carbon atoms to reduce the atomic density to the normal levels. The previous steps were repeated until perfect boundaries were obtained with 5-7 rings. This was then followed by energy minimization simulation using the conjugate gradient algorithm to obtain CNTs with optimized configurations. The minimized structure of a CNT was considered to be optimized once the change in the total potential energy (PE) of the system between subsequent steps is less than $1.0 \times 10^{-10}$ kcal/mol. Subsequently, MD simulations were performed in the NVT ensemble at an interval of 0.5 fs for 50 ps to equilibrate the CNT structures, where the velocity Verlet algorithm...
was used to integrate the equations of motion. Finally, a uniaxial tension simulation was performed by fixing one end of the CNT and applying a constant speed of 0.1 Å/ps at the other end. This corresponds to a nominal strain rate in the conducted MD simulations of $1.25 \times 10^9$ s$^{-1}$. This is typical of MD simulations in Refs. [49-52] in which very high strain rates up to $1 \times 10^{10}$ s$^{-1}$ were applied. The strain rate used in our simulations allowed us to ensure the equilibrium of the CNT’s atomic structure [53], and hence capture the true response of the CNT. The atoms of the moving end were also constrained in the transverse plane to prevent the loaded CNT from bending at high loads. The atoms of the CNT between the two ends were equilibrated during the simulation in the NVT ensemble at 300 K. The reaction forces on the fixed end atoms were calculated throughout the simulation and then used to obtain the stress-strain curve. The tensile simulation was stopped when the CNT was completely fractured. Young’s modulus of the CNT was calculated from the initial slope of the stress-strain curve and the averaged stresses were calculated assuming a uniform tensile stress distribution along the cross-sectional area of the CNT:

$$\sigma_{\text{axial}} = \frac{F_{\text{reaction}}}{\pi D_{\text{CNT}} t_{\text{CNT}}}$$

where, $F_{\text{reaction}}$ is the summation of all reaction forces along the CNT axis at the fixed end, and $D_{\text{CNT}}$ and $t_{\text{CNT}}$ are the respective averaged diameter and thickness of the CNT.

### 6.5 Results and discussions

We carried out comprehensive MD simulations to determine Young’s moduli of polycrystalline CNTs subjected to axial extension, focusing on the effects of grain size and orientation. Figure 7.6 shows the comparison of the stress–strain curves obtained for CNTs with random GBs, constructed in three different ways (see Table 6.1 for details). The corresponding energy curves for the three samples are demonstrated in Fig. 6.7. We also considered pristine (19, 19) CNT to compare the results with those for polycrystalline CNTs. This armchair CNT is the nearest pristine nanotube in diameter to the considered polycrystalline cases. Initially, the gradient of the stress-strain curves increases as the applied axial load increases. The slope of the stress-strain curve in this range provides Young’s modulus. We determined the averaged Young’s modulus of a CNT made of random GBs using the data from the three different MD tests. In a similar fashion, the
averaged Young’s moduli were obtained for all other cases; namely, three MD runs were conducted of CNT with helical GB, parallel GB with respect to CNT axis and transverse GB relative to CNT axis, as shown in Fig. 6.8. Table 6.2 summarizes the obtained results. This table also lists the fracture strength, failure strain and PE for all cases, which will be discussed in detail in the next section.

![Stress-strain curves of the pristine CNT and polycrystalline CNTs with random GBs (corresponding to first 4 rows of Table 6.1).](image1)

**Figure 6.6** Stress-strain curves of the pristine CNT and polycrystalline CNTs with random GBs (corresponding to first 4 rows of Table 6.1).

![The variation of the PE of CNTs with random GBs (corresponding to rows 2 to 4 of Table 6.1).](image2)

**Figure 6.7** The variation of the PE of CNTs with random GBs (corresponding to rows 2 to 4 of Table 6.1).
Figure 6.8 Averaged stress-strain curves of pristine and polycrystalline CNTs.

Table 6-2 Comparisons of mechanical properties and potential energy (PE) of different polycrystalline CNTs

<table>
<thead>
<tr>
<th>CNT Type</th>
<th>Young’s Modulus (GPa)</th>
<th>Fracture strength (GPa)</th>
<th>Fracture strain (%)</th>
<th>PE/atom (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine (19,19)</td>
<td>936.2</td>
<td>103.2</td>
<td>18.9</td>
<td>-7.310</td>
</tr>
<tr>
<td>Random GBs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample #1</td>
<td>739.4</td>
<td>50.1</td>
<td>-7.24</td>
<td>-7.240</td>
</tr>
<tr>
<td>Sample #2</td>
<td>719.3</td>
<td>54.2</td>
<td>-7.207</td>
<td>-7.207</td>
</tr>
<tr>
<td>Sample #3</td>
<td>657.3</td>
<td>41.6</td>
<td>-7.222</td>
<td>-7.222</td>
</tr>
<tr>
<td>Average</td>
<td>705.3</td>
<td>48.6</td>
<td>-7.223</td>
<td>-7.223</td>
</tr>
<tr>
<td>Parallel GBs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample #1</td>
<td>868.2</td>
<td>49.9</td>
<td>-7.236</td>
<td>-7.236</td>
</tr>
<tr>
<td>Sample #2</td>
<td>832.5</td>
<td>68.6</td>
<td>-7.261</td>
<td>-7.261</td>
</tr>
<tr>
<td>Sample #3</td>
<td>819.9</td>
<td>52.8</td>
<td>-7.261</td>
<td>-7.261</td>
</tr>
<tr>
<td>Average</td>
<td>840.2</td>
<td>57.1</td>
<td>-7.253</td>
<td>-7.253</td>
</tr>
<tr>
<td>Helical GB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample #1</td>
<td>802.1</td>
<td>44.1</td>
<td>-7.264</td>
<td>-7.264</td>
</tr>
<tr>
<td>Sample #2</td>
<td>785.8</td>
<td>44.8</td>
<td>-7.276</td>
<td>-7.276</td>
</tr>
<tr>
<td>Sample #3</td>
<td>868.9</td>
<td>45</td>
<td>-7.278</td>
<td>-7.278</td>
</tr>
<tr>
<td>Average</td>
<td>818.9</td>
<td>44.6</td>
<td>-7.273</td>
<td>-7.273</td>
</tr>
<tr>
<td>Transverse GB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample #1</td>
<td>712.5</td>
<td>39.3</td>
<td>-7.219</td>
<td>-7.219</td>
</tr>
<tr>
<td>Sample #2</td>
<td>837.6</td>
<td>44.3</td>
<td>-7.245</td>
<td>-7.245</td>
</tr>
<tr>
<td>Sample #3</td>
<td>718.2</td>
<td>39.5</td>
<td>-7.267</td>
<td>-7.267</td>
</tr>
<tr>
<td>Average</td>
<td>756.1</td>
<td>41</td>
<td>-7.244</td>
<td>-7.244</td>
</tr>
</tbody>
</table>

The results of Table 6.2 show a noticeable reduction in Young’s modulus of the polycrystalline CNTs in comparison with the pristine single-crystal CNT for which Young’s modulus (E) is ~936 GPa. This reduction results from the presence of GBs which manifest themselves highly localized...
defects and fracture initiation sites. We can also observe that the values of \( E \) are strongly dependent on the orientation of GBs. Among all other types of GBs listed in Table 6.2, random GBs are found to drastically reduce the averaged value of \( E \) by some 25\% in comparison with the pristine CNT. This significant reduction in CNT strength is attributed to the presence of the grain boundary triple junctions and the larger interactions between the stress fields of the pentagon–heptagon defects. On the other hand, the reduction in \( E \) was found to be only \( \sim 10\% \) of the pristine tubes in the case of parallel GB. This is attributed to the equal sharing of axial load by the two halves of the polycrystalline CNT. It is also worth noting that interactions between the stress fields of the pentagon–heptagon defects along the GBs were found to be less prominent. The other two cases of orientations of GBs (i.e. helical and transverse) fall in between these extreme values of \( E \), and the reductions were found to be around 12.5\% and 19\%, respectively. Unlike the parallel case, in the horizontal case, the entire load is fully transmitted through the circumferential GB, and thus the strength of a CNT is fully controlled by the weak 5-7 defects. In the case of polycrystalline graphene, several researchers [18, 21, 31, 34] reported that the orientation angle of GBs and dislocation types do not much influence the mechanical performance of graphene, which is in contrast to our findings. This is due to the variation of the included angles of C–C bonds of a polycrystalline CNT with its radius. When a polycrystalline graphene sheet forms a CNT structure, the lengths and the spatial relations of the C–C bonds change. It may also be noted that the grain size does not much affect the elastic modulus of CNTs; rather, the orientations of the GBs play a critical role in dictating the elastic properties of the CNTs.

### 6.5.1 Failure behavior of polycrystalline CNTs

The fracture of polycrystalline CNTs was explored by performing MD simulations using realistic finite-grain-size models, emphasizing the role of orientations of GBs. GBs may act as initiation sites and the potential precursor of their ultimate fractures. Therefore, we hypothesize that C-C bond along the GBs would ultimately lead to the fracture of CNTs, serving as accumulators of prestrain and consequently reducing the CNT strength. It provides us additional motivation to explore the role of GBs and grain sizes on the fracture strength of the polycrystalline CNTs. Figure 7.9 shows snapshots of the polycrystalline CNT with random GBs at different stages of the tensile test simulation illustrating the initiation and propagation of cracks along GBs that lead eventually to the complete fracture of the CNT. Figures 6.9 (a) and (b) show the respective snapshots of the
CNT before and after applying uniaxial strain of 7% just prior to crack initiation. The out-of-plane deformations (i.e. ripples) at the GBs undergo a straightening process during tension as shown in Fig. 6.9 (b). Figure 6.9 (c) shows that fracture initiates at the triple junction of GBs due to the associated high stress concentration at that junction and the failure of the weak 5-7 rings that progresses along the GB. Analogous behavior was observed in all other cases as well, since the internal grain structures of a CNT are defect-free. Once a crack initiation site is established, the crack extends in an intergranular manner depending on the orientations of the GBs. Figure 6.9 (d) shows a completely fractured CNT with some dangling carbon atoms.

Figure 6.9 Simulation of failure of a CNT with random GBs under tensile loading. (a) Unstrained CNT, (b) CNT strained under tension at an average strain rate of $1.25 \times 10^9$ s$^{-1}$. (c) Fracture nucleates at GB and the interiors of the grains remain stress free. (d) A global fracture of a CNT.

We refer to the tensile stress-strain curves for polycrystalline CNTs presented in Figs. 6.6 and 6.7. As the applied strain is further increased, the polycrystalline CNT fails due to the crack nucleation and propagation along the GB. From Fig. 6.8, it can be observed that the orientation of GBs significantly affects the failure behaviour of the CNTs. Transverse GB has detrimental influence on the fracture strength ($\sigma_f$) of a CNT and reduces the value of $\sigma_f$ by some 60%. On the other
hand, the presence of parallel GB in the CNT reduces the value of \( \sigma_f \) by around 46% in comparison with the pristine CNT. Interestingly, these two cases have the same number of grains with identical grain size provide a counterintuitive finding. The fracture strength of CNTs with all other orientations of GBs lies within the transverse and parallel GBs cases. It can also be observed from Figs. 6.6 and 6.8 that a trade-off exists between the values of \( E \) and \( \sigma_f \) in case of random and transverse GBs. The respective values of \( E \) and \( \sigma_f \) are 705 GPa and 48.6 GPa in the case involving random GBs, while in the case involving a transverse GB, they are 756 GPa and 41 GPa, respectively. This trade-off is caused by the difference in the CNT response during deformation depending on the GBs content and orientation, which leads to different nonlinear behavior at high strains. This clearly shows an opportunity for tailoring the mechanical properties of polycrystalline CNTs by engineering the GBs. From the listed values of the failure strains in Table 6.2, we can observe the brittle (catastrophic) fracture of the polycrystalline CNTs. On the contrary, the pristine CNT shows signs of ductile fracture as manifested by the large fracture strains. This is due to the fact that dislocations that develop along the GBs in polycrystalline CNTs are completely sessile, and brittle breakage of sp\(^2\) bonds dominates the failure behavior rather than dislocation movement. This finding is in good accord with the brittle fracture of polycrystalline graphene systems [18, 21, 34].

### 6.5.2 Effect of curvature on the mechanical properties of polycrystalline CNTs

We investigated the effect of nanotube’s curvature on the mechanical properties of polycrystalline CNTs with horizontal GB of different diameters ranging from 9 Å to 24 Å [see Figs. 6.5 (a) to (c)]. We also compared the obtained results of polycrystalline CNTs with those of pristine CNTs of similar diameter and unfolded graphene sheet of a CNT of 24 Å diameter [see Fig. 6.4(d)]. Table 6.3 summarizes the obtained results from the tensile MD simulations for all cases considered. It is very clear that the diameter significantly influences the mechanical properties of polycrystalline CNTs. For instance, the elastic modulus, the fracture strength and the fracture strain decreased by 14.8%, 24.3%, and 19.6%, respectively, corresponding to the diameter of a polycrystalline CNT of 9 Å, 16 Å and 24 Å. On the other hand, the mechanical properties of pristine armchair CNTs were found to slightly decrease (~2%) with increasing CNT diameter. The significant reduction in the properties of polycrystalline CNTs is attributed to the
development of surface irregularities leading to buckling of their cylindrical surface, which eventually distributes the load non-uniformly along the nanotube circumference. Figures 6.10(a) to (c) show snapshots of the grains and hexagons located at each side of the GB of three different CNTs. The mechanical properties of the polycrystalline graphene sheet representing the unfolded polycrystalline CNT of diameter ~ 24 Å were also determined and compared with those of a pristine graphene sheet. The results show that the elastic modulus of the polycrystalline CNT is ~22% higher than that of the unfolded graphene sheet. On the other hand, the polycrystalline graphene sheet undergoes ~28% more deformation before it fractures in comparison to the CNT. Furthermore, the cohesive energy per atom was found to increase with the increase in the CNT diameter. However, the cohesive energy per atom for the unfolded graphene sheet was found to be lower when compared with the rolled CNT, this is attributed to the higher number of carbon atoms that exist at the sheet boundaries with unpaired electrons. We calculated the cohesive energy per atom for a larger graphene sheet (500 Å × 500 Å) and found it to be -7.336 eV/atom.

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Chirality/defect type</th>
<th>Young’s modulus (GPa)</th>
<th>Fracture strength (GPa)</th>
<th>Fracture strain (%)</th>
<th>PE/atom (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT with horizontal GB</td>
<td>D = 9.0 Å</td>
<td>892</td>
<td>59.28</td>
<td>7.05</td>
<td>-7.231</td>
</tr>
<tr>
<td>CNT with horizontal GB</td>
<td>D = 16.0 Å</td>
<td>841.5</td>
<td>47.94</td>
<td>5.69</td>
<td>-7.274</td>
</tr>
<tr>
<td>CNT with horizontal GB</td>
<td>D = 23.75 Å</td>
<td>759.8</td>
<td>44.80</td>
<td>5.67</td>
<td>-7.276</td>
</tr>
<tr>
<td>Pristine CNT</td>
<td>n = m = 7</td>
<td>838.27</td>
<td>103.04</td>
<td>19.65</td>
<td>-7.256</td>
</tr>
<tr>
<td>Pristine CNT</td>
<td>n = m = 12</td>
<td>825.79</td>
<td>104.01</td>
<td>19.56</td>
<td>-7.290</td>
</tr>
<tr>
<td>Pristine CNT</td>
<td>n = m = 18</td>
<td>821.12</td>
<td>104.66</td>
<td>19.74</td>
<td>-7.301</td>
</tr>
<tr>
<td>Graphene with horizontal GB</td>
<td>Loading in Vertical direction</td>
<td>589.8</td>
<td>42.97</td>
<td>7.27</td>
<td>-7.242</td>
</tr>
<tr>
<td>Pristine graphene</td>
<td>Loading in the armchair direction</td>
<td>898.8</td>
<td>93.06</td>
<td>15.12</td>
<td>-7.286</td>
</tr>
</tbody>
</table>
6.5.3 Effect of temperature on the mechanical properties of polycrystalline CNTs

We further investigated the effect of temperature on the mechanical properties of polycrystalline CNTs of diameter 9 Å. For such an investigation, we performed uniaxial tensile MD simulations at different temperatures ranging from ~0 K to 10700 K. Figures 6.11 (a) and (b) show the...
variation of the PE and uniaxial stress of the CNT under uniaxial strain at different temperatures. The temperature was found to significantly influence the fracture strength and the fracture strain. The relationships between the temperature and the fracture properties were obtained by curve fitting the results with linear functions, as depicted in Figs. 6.12 (a) and (b).

![Graphs showing the variation of fracture strength and strain with temperature](image)

**Figure 6.12** The variation of (a) the fracture strength and (b) the fracture strain with temperature of CNT with circumferential GB of diameter 9 Å.

### 6.6 Conclusions

In this study, which is the first of its type, we performed systematic and comprehensive MD simulations to determine the mechanical properties of polycrystalline CNTs subjected to axial extension. An algorithm was developed to generate the atomistic descriptions of polycrystalline CNTs with a variety of GB types using Voronoi tessellation technique. The mechanical strength and the fracture behaviour of polycrystalline CNTs were explored by conducting MD simulations with varied finite-grain-size models, emphasizing the role of orientations and size of grains. Contrary to existing studies of polycrystalline graphene, we found that the mechanical performance of CNTs is largely governed by the orientations of GBs but not the size of the grains. For instance, our simulations reveal a ~60% strength reduction due to the presence of transverse GBs in a CNT, with cracks initiating at the GBs. On the other hand, GBs aligned with the axis of a CNT were found to be less detrimental to the mechanical properties in comparison to all other orientations of GBs. Trade-off between Young’s modulus and the fracture strength was also
observed for a particular type of GB orientation. The results show a significant dependence of the properties of polycrystalline CNTs on the nanotube curvature, diameter and temperature. The current results show that GBs are important intrinsic defects in CNTs which can be engineered and used to tailor the properties of functional devices.

6.7 Acknowledgements

This work was fully supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). S.I.K. acknowledges the generous support of the Banting Postdoctoral Fellowship program.

6.8 References

PART II

Atomistic Modeling of Interfacial Properties of CNT-Reinforced Polymer Composites

Summary: In the second part of this thesis, we investigated the interfacial properties of CNT-reinforced epoxy composites using pull-out atomistic simulations. The conducted work in this subject is presented in the next two chapters. As this is a non-traditional format paper-based thesis, each chapter has been written in the form of a journal paper. All similarities with papers presented in previous chapters were omitted to avoid unnecessary duplication. In Chapter 7, we investigated the effects of CNT diameter and length, interface layer thickness, and LJ cut-off distance on the interfacial shear strength of CNT-epoxy composites. The obtained results from this investigation were compared with those obtained using the atomics based continuum technique. In Chapter 8, the influence of dispersion state and morphology of CNTs on the interface strength was investigated. The waviness effect was considered by modeling CNTs with a wide range of curvatures ranging from straight to severely curved, while the agglomeration effect was considered by modeling hexagonal bundles of CNTs. The obtained results from this investigation were used to obtain a generalized relation for the interfacial shear strength of nanocomposites.
Chapter 7.
Paper #5: Interfacial and Mechanical Properties of Epoxy Nanocomposites Using Different Multiscale Modeling Schemes

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7.1 Abstract

In this study, we investigate the interfacial properties of carbon nanotube (CNT) reinforced epoxy composite. We conducted molecular dynamics (MD) simulations to determine the atomic-level interfacial properties of a representative volume element (RVE) comprised of CNT-epoxy composite. The work was further extended and used atomistic-based continuum (ABC) multiscale modeling technique, which makes use of constitutive relations derived solely from interatomic potentials to model the same system. Interestingly, the results of our comparative investigation revealed that (i) the ABC technique and MD simulation provided almost identical predictions for the atomic-level interfacial properties of the considered nanocomposite systems, (ii) the predicted ISS by the MD and ABC techniques agreed well with each other for a wide range of structural and geometrical parameters, (iii) both modeling approaches indicated that the increase in the length of a CNT leads to a decrease in the values of ISS of the resulting nanocomposite, and (iv) the values of the ISS of a nanocomposite system increase with the LJ cut-off distance and become stabilized at higher cut-off value,

Keywords: Multiscale modeling; Molecular dynamics; Atomistic-based continuum; Carbon nanotube; Interfacial properties; Mechanical properties


7.2 Introduction

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

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

A significant number of analytical and numerical studies have also been conducted to investigate the interfacial properties of CNT-based composites. For example, Lordi and Yao [19] used force-field based molecular mechanics calculations to determine the binding energies and sliding frictional stresses between CNTs and a range of polymer substrates, in an effort to understand the
factors governing interfacial strength. They reported that binding energies and frictional forces play only a minor role in determining the strength of the interface, but that helical polymer conformations around the CNT are essential in developing high ISS. Liao and Li [20] studied the interfacial characteristics of a CNT-reinforced polystyrene composite system through molecular mechanics simulations and elasticity calculations. They reported that the CNT-matrix bonding arises from non-bonded electrostatic and van der Waals (vdW) interactions, deformation induced by these interactions, and mismatch in the coefficients of thermal expansion. Their CNT pull-out simulation results suggest that the interfacial shear stress of the CNT-polystyrene system is about 160 MPa; significantly higher than conventional carbon fiber composite systems. Frankland et al. [21] generated stress–strain curves of polyethylene nanocomposite reinforced with long and short CNTs using MD simulations. Both nanocomposites were mechanically loaded in the axial and the transverse directions of the CNT axis. In their study, nanocomposite reinforced with long CNTs showed an increase in the stiffness relative to the polymer. On the other hand, nanocomposites reinforced with short CNTs showed no enhancement relative to the polymer. Xiao and Zhang [22] studied the effects of CNT length and diameter on the distributions of the tensile stress and interfacial shear stress of a CNT in an epoxy matrix. Their work revealed that a smaller CNT diameter has a more effective reinforcement effect and that there exists an optimal tube length at which reinforcement is maximized. They also reported that a CNT has a greater stress transfer efficiency than a solid fiber and provides toughness and tensile strength to the resulting nanocomposite. An analytical model has been developed by Haque and Ramasetty [23] to study the axial stress and shear stress at the interface of CNT-reinforced polymer composite materials. An expression for the effective length of the CNT has also been established by them for studying the load transfer efficiency in CNT-reinforced composites. A micromechanics model has also been developed by Li and Saigal [24] for assessing the interfacial shear stress transfer in CNT-reinforced polymer composites. Their results indicate that the stress transfer characteristics of nanocomposites can be improved by using sufficiently long CNTs. The load transfer efficiency in the CNT-reinforced nanocomposites was investigated by Tsai and Lu [25] using the conventional shear lag model and the finite element analysis. They revealed that the load transfer efficiency increases with the increment of the aspect ratio of CNTs. Using finite element model, Shokrieh and Rafiee [26] studied the tensile behavior of embedded short CNTs in the polymer matrix in presence of vdW interactions in interphase region. They modeled the interphase using non-linear spring elements capturing the force-distance curve of vdW interactions. They observed
that improvement in the Young’s modulus of CNT-reinforced composite is negligible for lengths smaller than 100 nm and saturation takes place in larger lengths on the order of 10 µm.

7.3 Molecular Dynamics Modeling and Simulations

This Section is devoted fully to molecular dynamics modeling and simulations. All MD runs were conducted with the aid of large-scale atomic/molecular massively parallel simulator (LAMMPS) [27] by using the consistent valence force field (CVFF) [28]. Conjugate gradient algorithm was used to minimize the total potential energy of the initial configurations, while velocity Verlet algorithm was used to integrate the equations of motion in all MD simulations. Periodic boundary conditions were imposed on all directions of the MD unit cells. In the simulations, the non-bonded interactions between the atoms are represented by vdw interactions and Coulombic forces.

7.3.1 CNT-Epoxy Interface Layer Thickness

The structure of the epoxy matrix at the vicinity of the CNT surface differs from the bulk epoxy due to the formation of an ultra-thin epoxy layer at the CNT-epoxy interface. This ultra-thin layer at the CNT-epoxy interface, which is ignored by many researchers, consists of a highly packed crystalline polymer, which has higher elastic properties than the amorphous bulk polymer [18,29]. In order to obtain the actual CNT-epoxy properties, the size of the RVE must be large enough to incorporate the change of the polymer structure. The cylindrical molecular structure of the CNT is treated as an equivalent solid cylindrical fiber [30–32] for determining its volume fraction in the nanocomposite RVE,

\[
\text{CNT volume fraction} = \frac{L_{\text{CNT}} \times \pi \left( \frac{d_{\text{CNT}} + h_{\text{vdW}}}{2} \right)^2 - \left( d_{\text{CNT}} - t_{\text{CNT}} \right)^2}{\nu} \tag{7.1}
\]

where \( d_{\text{CNT}} \), \( L_{\text{CNT}} \) and \( t_{\text{CNT}} \) denote the respective diameter, length and thickness of a CNT, and \( h_{\text{vdW}} \) is vdw equilibrium distance between the CNT and the surrounding polymer matrix.
To determine the thickness of the interface layer, we performed a MD simulation for a system consisting of a CNT of length 43.0 Å surrounded by 51 epoxy oligomers. The size of the periodic RVE was 50 Å × 50 Å × 43 Å and its details are summarized in Table 7.1. Subsequently, the RVE is equilibrated using the same modeling steps as described above for pure epoxy. Figure 7.1 shows the radial distribution function (RDF) of the epoxy atoms that surround the CNT after the equilibration process.
equilibration. The variation of the RDF along the radial direction represents the change of the epoxy structure in the vicinity of the embedded CNT. It may be observed from Fig. 7.1 that the RDF of epoxy atoms is zero at the radial distance of 8 Å and reaches its maximum value of 360 atoms/nm³ at the radial distance of 9.5 Å. Then, it starts to fluctuate around an average value of 225 atoms/nm³. Fig. 7.2 shows a close view of the equilibrated RVE. The obtained values of the interface thickness and the equilibrium separation distance were used in the following sections to select the appropriate RVE size.

<table>
<thead>
<tr>
<th>Table 7-1 Parameters used in the RVEs.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>CNT type</td>
</tr>
<tr>
<td>CNT diameter (Å)</td>
</tr>
<tr>
<td>CNT length (Å)</td>
</tr>
<tr>
<td>RVE dimensions (Å³)</td>
</tr>
<tr>
<td>CNT volume fraction</td>
</tr>
<tr>
<td>Total number of atoms</td>
</tr>
</tbody>
</table>

7.3.2 CNT Pull-out Simulations

Amongst the most common approaches for measuring the ISS of the CNT-polymer nanocomposite is the pull-out test. During the pull-out simulations, one-end of the fully embedded CNT is extracted from the matrix at constant pull-out rate or velocity of 1×10⁻⁵ Å/fs in the NVT ensemble at 300 K [33]. The periodic boundary conditions were removed along the axial direction of the CNT and the matrix was constrained during the pull-out simulation [34]. The pull-out force and the average ISS were then determined based on the work done during the pull-out test. Typical snapshots during CNT pull-out from epoxy matrix are depicted in Fig. 7.3.

7.4 Atomistic-Based Continuum (ABC) Modeling

Recently, Meguid and coworkers [35,36] presented novel ABC modeling schemes to investigate the interfacial and mechanical properties of CNT-reinforced polymer composites. In their works, the problem is formulated by using a RVE which consists of the reinforcing CNT, the surrounding polymer matrix, and the CNT/polymer interface as demonstrated in Fig. 7.4. The idea behind the ABC technique is to incorporate atomistic interatomic potentials into a continuum framework. In
this way, the interatomic potentials introduced in the model to capture the underlying atomistic behaviour of the different phases considered. Thus, the influence of the nanophase is taken into account via appropriate atomistic constitutive formulations. For the sake of completeness, we provide a brief outline of this technique detailed in their work [35,36].

Figure 7.3 Schematics of CNT-reinforced epoxy composite at various displacements during CNT pull-out process.

Fundamental to their proposed concept is the notion that a CNT is a geometrical space-frame-like structure and the primary bonds between two nearest-neighboring atoms act like load-bearing beam members. As in traditional FE models, nodes are used to connect the beam elements to form the CNT structure. In this case, the nodes represent the carbon atoms and are defined by the same atomic coordinates. They adopted the Modified Morse interatomic pair potential with an added angle bending term to describe the atomic interactions in the CNT. The parameters used for the potential in their study are the same as those adopted by Belytschko et al. [37]. The Modified Morse potential is given by:

\[ E = E_s + E_b \]  

\[ E_s = D_e \left( 1 - \exp^{-\beta(r-r_o)} \right)^2 - 1 \]
\[ E_b = \frac{1}{2} k_\theta (\theta - \theta_o)^2 [1 + k_{\text{sxtic}} (\theta - \theta_o)^4] \] (7.4)

where \( r_o \) is the initial bond length, \( \theta_o \) is the initial angle between adjacent bonds, \( D_e \) is the dissociation energy, \( \beta \) is a constant which controls the ‘width’ of the potential, and \( k_\theta \) and \( k_{\text{sxtic}} \) are the angle bending force constants.

Figure 7.4 Schematic of the RVE [35].

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

\[ F = 2\beta D_e (1 - \exp^{-\beta r}) \exp^{-\beta r} \] (7.5)

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

\[ M = k_\theta \Delta \theta [1 + 3k_{\text{sxtic}} (\Delta \theta)^4] \] (7.6)
which represents the moment required to bend neighboring bonds. Again, this expression is used to define the stiffness of the rotational spring elements throughout the simulation. The LJ interatomic potential is used to describe the vdW interactions at the CNT/polymer interface. The LJ potential is defined as

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

(7.7)

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

They adopted the ABC technique to explicitly model each interaction across the interface using the concept of continuum elements. In this case, each atomic interaction is represented by a continuum truss rod which extends out from a carbon atom in the CNT structure to an atom in the epoxy matrix. The LJ parameters for the interactions considered in their work are summarized in Table 7.2.

<table>
<thead>
<tr>
<th>LJ interaction</th>
<th>(\mu) (J)</th>
<th>(\psi) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon–carbon (C–C)</td>
<td>(3.89 \times 10^{-22})</td>
<td>3.4</td>
</tr>
<tr>
<td>Carbon–hydrogen (C–H)</td>
<td>(4.44 \times 10^{-22})</td>
<td>3.2</td>
</tr>
<tr>
<td>Carbon–oxygen (C–O)</td>
<td>(4.90 \times 10^{-22})</td>
<td>3.2</td>
</tr>
<tr>
<td>Carbon–nitrogen (C–N)</td>
<td>(4.48 \times 10^{-22})</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Again, by differentiating the potential with respect to the separation distance, the following expression for the vdW force between two interacting atoms is obtained:

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

(7.8)

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. The epoxy was modeled by using higher ordered 3-D, 10-node solid tetrahedral elements with quadratic displacement behavior.
7.4.1 CNT Pull-out

Figure 7.5 shows a schematic of the displacement boundary conditions of the pull-out process. 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 force required to withdraw the CNT from the matrix is evaluated over the course of the pull-out process by summing the reaction forces at the upper CNT nodes. The corresponding ISS was determined by dividing the maximum pull-out force by the initial interfacial area, $A = \pi dl$, where $d$ and $l$ are the diameter and length of the embedded CNT, respectively.

![Figure 7.5 Polymer representation and pull-out boundary conditions [45].](image)

7.5 Results and Discussion

A series of MD simulations were carried out to determine the ISS of the nanoscale RVE reinforced with an individual CNT. The effects of such parameters as embedded CNT length, the thickness of the CNT-polymer interface, LJ cut-off distance and CNT diameter on the ISS are investigated and discussed. To investigate the effect of the pertinent parameters on the ISS, the same CNT type and its volume fraction in the RVE are considered as considered by Wernik et al. [36].

7.5.1 Effect of Embedded CNT Length

Five different CNT lengths were considered to compare the MD results with those of the ABC results. It is well known that a short length of CNT significantly influences the interfacial
characteristics of the resulting nanocomposite. Therefore, to reduce the computational effort, the maximum embedded CNT length in the polymer matrix is kept limited to 200 Å. Figure 7.6 shows the effect of embedded CNT lengths on the ISS of a nanocomposite with an interfacial thickness of 3.4 Å.

![Figure 7.6 Effect of embedded CNT length on the ISS.](image)

The ISS of the CNT-polymer composite system exhibits a decaying length trend similar to traditional fiber composites. It may also be observed that the ABC model slightly under predicts the ISS values. The subsequent MD simulations were carried out considering the embedded CNT length as being 200 Å.

### 7.5.2 Effect of CNT-Polymer Interfacial Thickness

In existing studies, the CNT-polymer interfacial thickness has not yet been unambiguously defined. Several different values have been used in both atomistic and continuum simulations. For instance, Hu et al. [38] simulated the helical wrapping of one polystyrene chain around a CNT considering only vdW interactions using MD simulations. The equilibrium distance between the hydrogen atoms in the polymer and carbon atoms in the CNT ranged from 2.851 Å to 5.445 Å. However, only one polymer chain was considered, while in practical cases there may be other chains which also wrap around the CNT. Montazeri and Naghdabadi [39] used an interfacial
thickness of 3.816 Å in their molecular structural mechanics model of CNT-reinforced polymer composites. This value corresponds to the equilibrium distance of the LJ potential. Hence, it is worthwhile to investigate the effect of different interfacial thicknesses on the ISS of CNT-reinforced polymer composite. Figure 7.7 shows the predicted ISS for the nanocomposite system for an interfacial thickness range of 2.2–4.25 Å.

![Graph showing effect of interfacial thickness on ISS](image)

**Figure 7.7** Effect of CNT-polymer interface thickness on the ISS.

This figure demonstrates that the ISS of the CNT-polymer composite system decreases with the increase in the interfacial thickness. This phenomenon is attributed to the fact that vdw interactions between the CNT and the epoxy become weaker with the increase in their atomic separation distance. The trend of this finding is also well confirmed by the ABC technique. In the ABC study, as the interfacial thickness is decreased, a larger number of polymer atoms were included in the computational cell which increases the number of vdw interactions occurring over the interface and the subsequent ISS. Comparative trends also suggest that MD approach slightly overestimates the values of ISS over the ABC technique for the higher interfacial thicknesses. The subsequent MD simulations were carried out considering the CNT-polymer interfacial thickness as being 2.2 Å.
7.5.3 Effect of LJ Cut-off Distance

In most existing MD studies, the LJ interatomic potential used to simulate vdW interactions is often truncated to reduce the computational cost in such way that atom pairs whose distances are greater than the cut-off distance have zero vdW interaction energy. The cut-off distance is often taken to be 8.5 Å (see Ref. [36] and references therein). Truncating the potential introduces a sharp discontinuity between atoms inside and atoms outside the cut-off radius, particularly when smaller cut-off distances are used. Therefore, here an attempt is made to investigate the effect of LJ cut-off distance on the ISS of a nanocomposite. The LJ interatomic potential is defined in Eq. (12). The corresponding LJ parameters are listed in Table 7.3. Figure 7.8 shows the estimated MD results for a cut-off range of 6 Å to 13 Å. As expected, the values of ISS of a nanocomposite system increase with the LJ cut-off distance and become stabilized at higher cut-off distance (>12 Å). It may also be observed from Fig. 7.8 that both techniques predict the good agreement between the results for a wide range of cut-off distance.

![Figure 7.8 Effect of LJ cut-off distance on the ISS.](image-url)
Table 7-3 LJ potential parameters used in the present study.

<table>
<thead>
<tr>
<th>LJ interaction</th>
<th>μ (J)</th>
<th>ψ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>10.286 × 10^{-22}</td>
<td>3.617</td>
</tr>
<tr>
<td>C–H</td>
<td>5.213 × 10^{-22}</td>
<td>2.45</td>
</tr>
<tr>
<td>C–O</td>
<td>12.767 × 10^{-22}</td>
<td>2.859</td>
</tr>
<tr>
<td>C–N</td>
<td>11.607 × 10^{-22}</td>
<td>3.501</td>
</tr>
</tbody>
</table>

### 7.5.4 Effect of CNT Diameter

CNT diameter has a significant influence on the interfacial properties of the resulting nanocomposite. In this study, armchair CNT configurations are considered, with the smallest being a (5, 5) CNT, and the largest an (18, 18) CNT. Figure 7.9 demonstrates that the predicted ISS decreases approximately linearly with the increase in the value of the CNT diameter.

![Figure 7.9](image.png)

**Figure 7.9** Effect of CNT diameter on the ISS.

This finding demonstrates the advantage of using smaller diameter of armchair CNTs. Again, both multiscale modeling techniques (MD and ABC) show good agreement between the results for a wide range of CNT diameters. The marginal differences occur because an identical polymer configuration considered in the ABC study for all simulations in order to minimize the effect of polymer distribution on the pull-out curves.
7.6 Conclusions

In this article, we determined the interfacial properties of CNT-reinforced epoxy composites. Furthermore, we carried out a detailed comparison between the MD and ABC predictions considering pertinent parameters, such as embedded CNT length, thickness of the CNT-polymer interface, CNT diameter, LJ cut-off distance and orientations of dispersed CNTs. The following is a summary of our findings: (i) ISS results predicted by the MD and ABC techniques agree well with each other for a wide range of structural and geometrical parameters, (ii) both multiscale approaches indicate that the increase in the length of a CNT leads to a decrease in the values of ISS of the resulting nanocomposite, and (iii) the values of ISS of a nanocomposite system increase with the LJ cut-off distance and become stabilized at higher cut-off value.

7.7 References

Chapter 8.
Paper #6: Molecular dynamics simulations of the effect of waviness and agglomeration of CNTs on interface strength of thermoset nanocomposites

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8.1 Abstract

Most existing molecular dynamics simulations in nanoreinforced composites assume carbon nanotubes (CNTs) to be straight and uniformly dispersed within thermoplastics. In reality, however, CNTs are typically curved, agglomerated and aggregated as a result of van der Waal interactions and electrostatic forces. In this paper, we account for both curvature and agglomeration of CNTs in extensive molecular dynamic (MD) simulations. The purpose of these simulations is to evaluate the influence of waviness and agglomeration of these curved and agglomerated CNTs on the interfacial strength of thermoset nanocomposite and upon their load transfer capability. Two aspects of the work were accordingly examined. In the first, realistic carbon nanotubes (CNTs) of the same length but varied curvatures were embedded in thermoset polymer composites and simulations of pull-out tests were conducted to evaluate the corresponding interfacial shear strength (ISS). In the second, the effect of the agglomerate size upon the ISS was determined using bundles of CNTs of different diameters. The results of our MD simulations revealed the following. The pull-out force of the curved CNTs is significantly higher than its straight counterpart and increases further with the increase in the waviness of the CNTs. This is attributed to the added pull-out energy dissipated in straightening the CNTs during the pull-out process. It also reveals that agglomeration of CNTs leads to a reduction in the ISS and poor load transferability, and that this reduction is governed by the size of the agglomerate.
The simulation results were also used to develop a generalized relation for the ISS that takes into consideration the effect of waviness and agglomeration of CNTs of CNT-polymer composites.

8.2 Introduction

The mechanical performance of CNT-reinforced composites is significantly influenced by the interfacial properties between the dispersed CNTs and the surrounding matrix [1,2]. Higher interfacial shear stress (ISS) means better stress transfer from the polymer to the reinforcing CNTs [3]. Different parameters determine the reinforcement effect of the CNTs; including dispersion quality, alignment, existing defects, and morphology of the dispersed CNTs [4–6]. The impact of these parameters on the interfacial properties and the resulting mechanical properties were studied experimentally, theoretically, and numerically over the past decade [7]. For example, several experimental studies have been carried out to investigate the interfacial characteristics of CNT-reinforced composites using both direct methods such as pull-out or microdroplet tests, and indirect methods such as fragmentation test or Micro-Raman spectroscopy [8–10]. The ISS between CNTs and polymers was estimated to be as high as 500 MPa, which is more than one order of magnitude higher than those obtained in conventional composites [10]. In spite of these relatively high interfacial strength, the efficiency of stress transfer and hence the enhancement of the mechanical properties was lower than expected due to sliding of CNTs in the agglomerated bundles [8]. Cooper et al. [9] reported ISS in the range of 35 to 376 MPa. The large variation in these values was attributed to the inherent variances in the pull-out of CNTs, including embedded length, bundle size, and formation of covalent bonds between the CNT and the surrounding polymer along the interface. Wang et al. [11] estimated that the ISS of CNT-epoxy composites ranges from 79 to 93 MPa using microdroplet test. Zu et al. [12] found a linear relation between the debonding force and the embedded area of the CNT using microdroplet test. Their results exhibited some scattering due to the inherent irregularities in the pulled-out CNTs such as waviness and surface roughness. The predicted ISS was estimated to be 14.4 MPa by fitting the test results using the least-square method. An even lower ISS down to 3.5 MPa were measured for MWCNT-PEEK composite using a special AFM cantilever installed inside a SEM [13].

The full potential of CNTs as a reinforcement material is limited by the tendency of nanotubes to agglomerate and deform locally into wavy shapes [14,15]. Due to their high surface energy and
surface area, CNTs tend to agglomerate and aggregate into bundles [16,17]. The presence of agglomerates limits the stress transfer between the nanotubes inside the bundle and from the matrix to the CNTs, leading to a nanocomposite with inferior properties [8]. Due to their high aspect ratio and low bending stiffness, CNTs tend to bend or unfold when dispersed in polymer matrices [18]. The processing of such nanocomposites usually includes a mixing step that uses both mechanical steering and sonication processes to homogenously disperse nanotubes and breaks up any agglomerates in the prepared composites [19–21]. Due to the induced curvature, the elastic moduli of the nanotubes and consequently the nanocomposite will vary significantly in all directions [4]. For example, the reinforcing effect will increase in the transverse direction and decrease in the chord direction with increasing CNT curvature. The induced curvature of the dispersed nanotubes during mixing and sonication steps have harmful effects on the effective properties of the prepared nanocomposite [15].

Waviness and agglomeration of CNTs are inherent to the fabrication processes of CNT-reinforced composites [14]. Whilst determining their impact on the interfacial properties is essential in understanding how reinforcing mechanisms work, measuring it experimentally via direct Pull-out tests is challenging, especially when dealing with single wall carbon nanotubes (SWCNTs) [22]. As a result, different analytical and numerical techniques have emerged to handle this problem [23,24]. Chen et al. [25] developed an analytical model to study the effect of CNT waviness on the interfacial properties of CNT reinforced composites. They characterized the pull-out process into three consecutive stages: the bonded stage, the debonding stage, and the sliding stage. Their results showed that fibers with more curvature require more stress and energy to achieve a complete pull-out from the surrounding matrix. Later, they extended their work to investigate the effect of nanotube waviness on toughness properties by modeling crack bridging by curved CNTs [26]. In spite of the increase in the peak bridging stress for wavy CNTs, the overall toughness of the composite was found to decrease. Yazdchi et al. [27] developed a 3D analytical model for the pull-out of wavy CNTs. Their results showed that wavy CNTs have higher ISS compared with straight CNTs and that the ISS increases with increasing the nanotube’s curvature. It is noteworthy, however, that the many assumptions introduced in these analytical studies undermine the accuracy of their findings. Firstly, they neglect the discrete nature of CNTs by considering them as solid cylinders. Secondly, they assume CNTs to be homogenous, linearly elastic and isotropic. Thirdly, they assumed perfect bonding between the embedded nanotubes and the
polymer. On the other hand, MD simulations offer an appropriate and effective means to deal with these kinds of problems without having all these unnecessary assumptions [27,28], but at a computational cost.

Although the effect of nanotube waviness and bundle size on stiffness has been addressed previously using analytical modeling techniques, to the best of the authors' knowledge, no molecular dynamics simulations have been carried out to examine the influence of these parameters on the interfacial strength and the resulting toughness of the nanocomposite. Several studies have been conducted using MD to simulate the pull-out of straight individual [29,30] and agglomerated [31] CNTs from polymer matrix. We recently studied the effects of these parameters on the elastic properties of nanocomposite using molecular dynamics simulations [32,33]. In extension to that work, we now investigate the effect of CNT waviness and agglomeration on the interfacial properties by simulating the pull-out test using MD simulations. CNT bundles of different diameters are considered in the analysis to study the effect of the agglomerate size on the pull-out energy. Straight and wavy nanotubes of different curvatures are also modeled to study the effect of CNT waviness on the interfacial properties of CNT-reinforced composites. The pull-out force is calculated from the change in the potential energy of the system during the pull-out process and it is used later to calculate the ISS. The dispersion state and the morphology of the CNTs inside the polymer matrix is quantified using images obtained by a scanning electron microscope (SEM) and an atomic force microscope (AFM). The results of our research could be used to shed some light on the enormous scatter in the ISS values provided in the literature.

### 8.3 Molecular dynamics model

In order to design nanocomposites properly and optimize their properties, the effect of all variables, including nanotube waviness and agglomeration, on their performance must be considered. In our previous study [20], we covered the effect of CNT length, diameter, and orientation on the interfacial shear stress. Here, we extend this work to investigate the influence of CNT waviness and agglomeration using MD simulations. CNTs with different curvatures are assumed as reinforcements, while the agglomeration effect is captured by considering nanotube bundles of different diameters. Amongst the most common approaches for measuring the ISS of
the CNT-polymer nanocomposite is the pull-out test. Figure 8.1 shows a schematic representation of the pull-out model and the applied boundary conditions. The proposed model considers only weak bonding (van der Waal and electrostatic forces) between the embedded nanotubes and the surrounding matrix. Epoxy polymer based on DGEBA resin and TETA curing agent with resin/curing agent weight ratio set to 2:1 is used in the current work as the matrix [34,35]. The cross-linking and curing processes of the epoxy polymer were discussed and presented in detail in our previous study [19].

![Figure 8.1](image)

**Figure 8.1.** Schematic diagram showing the pull-out of partially embedded CNT from Epoxy matrix and the applied boundary conditions.

### 8.3.1 Modeling of curved CNT

Due to the relatively high aspect ratio of CNTs and their low bending stiffness; they tend to bend and form wavy nanotubes during manufacturing their nanocomposites (see Fig. 8.2). To address the effect of CNT waviness on the interfacial properties, MD simulations were conducted for representative volume elements (RVEs) reinforced with wavy nanotubes of different curvatures. In the proposed model, nanotubes curvature is described using a sinusoidal form; as follows:

\[
y = a \cos \left( \frac{2\pi z}{\lambda} \right) \text{ with } z \in [0, \lambda]
\]

where \( a \) and \( \lambda \) are the amplitude and the wavelength of the wavy nanotube, respectively [36]. The parameter \( \alpha = a/\lambda \) is the waviness ratio that defines the degree of curvature of the nanotube (see Fig. 8.3(a)). The waviness ratio, \( \alpha \), was determined via geometrical analysis of SEM and AFM.
images of a CNT/epoxy composite, as depicted in Fig. 8.2(a) and (b), respectively. Four shapes were selected to represent a wide range of CNTs curvatures, as shown in Fig. 8.3(b). Only half of a complete sine-curved nanotube was considered in the MD simulations. Three curved single wall carbon nanotubes were generated and equilibrated before using them as reinforcement fibers in the RVE of the nanocomposites. All nanotubes were selected to be (5,5) armchair SWCNT of length 270 Å and aspect ratio ~400, which are relatively high compared with earlier MD simulations [37,38]. The simulation region in each case was constructed by randomly placing the cross-linked epoxy structures around the embedded nanotube, as shown in Fig. 8.4. The size of the RVE in each case was adjusted in such a way that the CNT volume fraction in it remains constant at 1.2%. The details of the four RVEs examined are summarized in Table 8.1. The thickness of the epoxy in the radial direction was selected to be large enough so that the obtained results are independent of it [20].

Table 8.1 Parameters used in the RVEs with wavy (5,5) SWCNTs of length 270 Å at ~1.2 vol%.

<table>
<thead>
<tr>
<th>Case #</th>
<th>a (Å)</th>
<th>λ (Å)</th>
<th>α=a/λ</th>
<th>No of DGEBA Resins</th>
<th>No of TETA Curing agents</th>
<th>Total No. of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>∞</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>485</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>59</td>
<td>435</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>82</td>
<td>356</td>
<td>0.23</td>
<td>2760</td>
<td>1380</td>
<td>1.794×10⁵</td>
</tr>
</tbody>
</table>

Figure 8.2 Curved nanotubes in (a) an SEM micrograph of as-received CNTs and (b) an AFM micrograph of a CNT/epoxy composite.
8.3.2 Modeling of agglomerated CNTs

CNTs tend to agglomerate and aggregate into bundles due to their high surface energy and surface area (see Fig. 8.5). As a result, the reinforcement effects of the nanotubes decrease dramatically in the manufactured composite [39]. CNTs self-organize into crystalline bundles in the form of two-dimension hexagonal-packing arrangements [40]. The size of these bundles typically ranges from several to hundreds of CNTs [41]. The coupling between CNTs and the adjacent nanotubes within the bundle is weak, as it is mainly caused by van der Waal interactions [41]. The influence of CNT agglomeration on the interfacial properties of CNT-polymer composites was examined
in our study by simulating the pull-out of CNTs bundles from an epoxy matrix. In the agglomeration study, we assumed all CNTs to be straight neglecting the effect of nanotube waviness and entanglement.

The effect of agglomerate size was computed by simulating the pull-out of CNTs bundles of different diameters. Five RVEs were constructed to represent an epoxy matrix reinforced with: (i) a single CNT, (ii) a bundle of three CNTs, (iii) a bundle of seven CNTs, (iv) a bundle of nineteen CNTS, and (v) a bundle of thirty-seven CNTS, as shown in Fig. 8.6. All nanotubes are (5,5) armchair SWCNT of length 80 Å and aspect ratio ~118. The initial distance between the adjacent CNTs in each bundle is taken to be 3.4 Å, which is the intertube separation distance in multi-walled CNTs [42]. The details of the five RVEs are summarized in Table 8.2.

Figure 8.5 Agglomerated nanotubes in STEM micrographs of (a) as-received CNTs and (b) a CNT/PVP composite (After [43]).

Table 8-2 Parameters used in the RVEs reinforced with agglomerated (5,5) SWCNTs.

<table>
<thead>
<tr>
<th>Case #</th>
<th>No. of CNTs</th>
<th>No of DGEBA Resins</th>
<th>No of TETA Curing agents</th>
<th>Total No. of atoms</th>
</tr>
</thead>
<tbody>
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<td>164</td>
<td>82</td>
<td>11.18×10^3</td>
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<td>3</td>
<td>244</td>
<td>122</td>
<td>17.61×10^3</td>
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<td>7</td>
<td>326</td>
<td>163</td>
<td>25.46×10^3</td>
</tr>
<tr>
<td>4</td>
<td>19</td>
<td>1522</td>
<td>761</td>
<td>109.95×10^3</td>
</tr>
<tr>
<td>5</td>
<td>37</td>
<td>1654</td>
<td>827</td>
<td>130.3×10^3</td>
</tr>
</tbody>
</table>
Figure 8.6 Molecular models of epoxy matrix reinforced with: (a) single CNT, (b) bundle of three CNTs, (c) bundle of seven CNTs, (d) bundle of nineteen CNTs, and (e) bundle of thirty-seven CNTs.

### 8.3.3 MD simulation procedures

MD offers an appropriate and effective tool to deal with large systems and relatively longer simulation times compared to first principles methods [44,45]. We conducted MD simulations of the pull-out test of CNTs from epoxy matrix to determine the binding energy between them. The binding energy is equal to the change in the total potential energy of the system after the embedded nanotube is entirely pulled out. The work done by the pull-out force throughout the test is equal to the binding energy between the fully embedded CNT and the polymer. Knowing this, the pull-out force at any specific moment of the test can be calculated from the derivative of the binding energy function with respect to distance and the corresponding ISS can be simply determined by
dividing the maximum pull-out force by the total area of the interface. The complete procedure for conducting the pull-out simulations is done in as follows:

(i) Preparation: The initial structures of the epoxy and CNTs are separately equilibrated to their minimum energy structures using the conjugate gradient method. A specific number of the cross-linked epoxy structures are dispersed randomly around an individual wavy CNT or bundle of CNTs to build the nanocomposite system using Packmol package [46].

(ii) Compression: The initial simulation domain is gradually compressed into the targeted size. At the beginning of each compression stage, the coordinates of all atoms are remapped to fit inside the updated domain. The system coordinates are then optimized to reach the structure with the minimum potential energy. We annealed the obtained configuration by equilibrating it at room temperature in the constant temperature and volume canonical (NVT) ensemble over 200 ps with 0.5 fs time step using the velocity Verlet algorithm.

(iii) Equilibration: Another stage of equilibration is required to reach the atmospheric pressure and to relieve the induced residual stresses built up during the compression stage. This is achieved by equilibrating the system again for another 200 ps in the isothermal–isobaric (NPT) ensemble at 300 K and 1 atm. The obtained equilibrated system had a density of 1.1 gm/cm3.

(iv) Pull-out: Finally, all atoms at one one-end of the fully embedded CNT/CNT bundle is pulled-out from the matrix at a constant velocity of 1×10^(−4) Å/fs while the remaining atoms of the nanotube are equilibrated in the NVT ensemble at 300 K to calculate the potential energy of the system [38]. The periodic boundary conditions are removed along the pull-out direction, while the atoms of the polymer are fixed during the pull-out simulation [30].

Our MD simulations are conducted with large-scale atomic/molecular massively parallel simulator (LAMMPS) [47] using the consistent valence force field (CVFF) [48]. This force field is implanted in LAMMPS and has been successfully used by other researchers to predict the elastic and interfacial properties of CNT-epoxy composites [32,49].
8.4 Results and discussion

We conducted a series of MD simulations to determine the effect of CNT waviness and agglomeration on ISS of CNT-reinforced polymer composites. The effect of CNT waviness was studied by simulating the pull-out process of CNTs with different curvatures, while the effect of CNT agglomeration was investigated by simulating the pull-out process of CNT bundles of different sizes. In general, the value of the shear stress at the CNT-polymer interface determine the efficiency of stress transfer from the matrix to the embedded nanotubes [1]. These CNTs reinforce the matrix by sharing the applied load until either the failure of the interface or the fracture of the CNTs. The maximum shear stress that the interface can resist before the deboning starts is called the interfacial shear stress (ISS) and is used as a representative of the interfacial properties between CNTs and the polymer [1]. The binding energy between an embedded CNT and the surrounding polymer matrix is the difference between the total potential energy of the system before and after the pull-out:

$$\Delta PE = PE_{total} - (PE_{epoxy} + PE_{CNT})$$

where $PE_{total}$ is the total potential energy of the nanocomposite system, $PE_{epoxy}$ is the potential energy of the epoxy polymer without the CNT, and $PE_{CNT}$ is the potential energy of the CNT alone [31]. The variation of the pull-out force throughout the extraction process can be described in three stages: rapid escalating to the peak point which corresponds to the start of debonding, falling to an average value and continuing oscillating around this value during sliding from the matrix, and a breakdown stage in which the force drops down to zero upon exiting the matrix and the corresponding diminishing interactions between the leaving end of the nanotube and the nearest polymer atoms at the side of the matrix.

The work done by the pull-out force at any point is equal to the change in the potential energy of the system at this point [50]. Therefore, the pull-out force at any moment can be calculated from the derivation of the interfacial energy with respect to the axial distance at this moment. In the current analysis, the magnitude of the pull-out force throughout the MD simulation was approximated as the incremental change in the potential energy of the system every Angstrom:

$$F_{pull-out} = \frac{\Delta PE}{\Delta x}$$
Where $\Delta PE$ is the potential energy increment at each displacement increment $\Delta x=0.1$ nm [37]. Assuming uniform shear stress distribution along the interface area of the CNT, the average ISS can be calculated simply by balancing the forces:

$$ISS = \frac{F_{\text{pull-out}}}{\pi(D_{\text{CNT}} + h_{vdw})L_{\text{CNT}}}$$

(8.4)

where, $F_{\text{max}}$ is the maximum pull-out force recorded at the beginning of CNT deboning, $D_{\text{CNT}}$ is the CNT diameter, $L_{\text{CNT}}$ is the embedded fiber length, $h_{vdw}$ is the interfacial separation distance between the CNT and the epoxy, and $\pi(D_{\text{CNT}} + h_{vdw})L_{\text{CNT}}$ is the effective CNT interface area [50,51]. The magnitude of $h_{vdw}$ was estimated to be $\sim 2.5$ Å from the radial distribution function of the epoxy atoms at the vicinity of the embedded nanotube after reaching the equilibrium stage.

### 8.4.1 Effect of CNT waviness

Three MD simulations of the pull-out test of CNTs with different curvatures were conducted to determine quantitatively the effect of waviness ratio on the interaction/binding energy, pull-out force, and ISS of CNT-epoxy composites. The pull-out process was completed when the fully embedded nanotube was fully pulled out from the epoxy. Fig. 8.7 shows snapshots of the pull-out simulation of a curved CNT having a waviness ratio $\alpha=0.14$, where one end of the nanotube was pulled out with a constant velocity. In order to calculate the CNT-epoxy binding energy, the change in total potential energy of the system was computed throughout the simulations as a function of pull-out displacement for the four considered waviness cases, as shown in Fig. 8.8. The zero binding energy in Fig. 8.8 corresponds to a fully pulled out CNT from the epoxy matrix at a 270 Å displacement. The results show that the interfacial energy depends on the waviness ratio of the CNT. For higher CNT curvatures, the binding energy decreases rapidly at the beginning of the pull-out and then begins to decline steadily with the sliding from the epoxy until exiting the epoxy completely. Fig. 8.9 shows the variation of the pull-out force during the simulation. For straight CNTs, the applied pull-out force was only responsible for overcoming the non-bonded interactions between CNT’s atoms, and the surrounding polymer molecules. However, for curved nanotubes, an additional work is required, especially at the beginning to overcome the resistance of the curved nanotube against shape change and the accompanying change in the potential energy of the deformed CNT.
The pull-out of wavy CNTs from epoxy can be divided into three stages: initiation stage, unfolding-sliding stage, and final stage. The force required to initiate the pull-out process depends on the initial curvature of the CNT and was found to increase with the increase of the waviness ratio. However, this force drops to the same level required for straight CNTs after pulling the CNT out by ~2.5 nm. This pull-out stage is characterized by unfolding and sliding of the CNTs. Following the unfolding stage, the pull-out force fluctuates around an average value of 1.5 nN before falling down to zero in the final stage of the extraction. Thus, the pull-out force required to debond wavy CNTs can be simply described using the following equation:

\[ F_{\text{pull-out}} = F_{\text{vdW}} + F_{\text{wavy}} \]  

(8.5)

where, \( F_{\text{vdW}} \) is the force responsible for overcoming the van der Waals (vdW) interactions, and \( F_{\text{wavy}} \) is the force required to straighten the curved nanotube. In the present study, only non-bonded interactions were considered assuming pristine CNTs. A third part can be added to the above equation if the effect of chemical functionalization was considered via adding some covalent bonds between the CNT and the polymer. The obtained pull-out forces were used in Eq. (8.3) to calculate the average ISS. Table 8.3 summarize the results obtained for the three waviness cases.
Table 8-3 Pull-out energies and shear stresses in the 3-tube rope/epoxy resin composites.

<table>
<thead>
<tr>
<th>Case #</th>
<th>Waviness ratio (α)</th>
<th>Binding energy (Kcal/mol)</th>
<th>Max. Pull-out force (nN)</th>
<th>ISS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>3207</td>
<td>3.0</td>
<td>41.2</td>
</tr>
<tr>
<td>2</td>
<td>0.07</td>
<td>3855</td>
<td>7.5</td>
<td>103.5</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>3608</td>
<td>9.3</td>
<td>127.2</td>
</tr>
<tr>
<td>4</td>
<td>0.23</td>
<td>3382</td>
<td>10.8</td>
<td>148.0</td>
</tr>
</tbody>
</table>

Figure 8.8 Binding energy plots during the pull-out of CNTs with different curvatures from epoxy matrix as a function of pull-out displacement.

An approximate function relating the waviness ratio of CNTS and the ISS is obtained by curve fitting the simulation results:

\[ ISS = 13211 \alpha^3 - 6713 \alpha^2 + 1295 \alpha + 41.2 \]  

Equation 6 indicates a third-order polynomial relationship between the ISS and the waviness ratio, \( \alpha \), of the CNT, signifying the significant impact of the morphology of the dispersed nanotubes on the interfacial properties of the nanocomposite. These predictions agree with the experimental results of Zhang et al. [52] in which the CNT curvature was found to cause a significant increase over a straight CNT in the interwall friction during the pull-out of the inner tube from the outer tube in double-walled CNTs. The interwall friction was also noted to increase with the increase
of the nanotube curvature. However, the influence of waviness on the toughness of the nanocomposite at the bulk level needs further investigation. For example, Chen et al. [26] found analytically that the effective toughness of the nanocomposite deteriorates due to the accompanying decrease in average pull-out length and effective stiffness of the CNT [15,53,54].

![Graph showing pull-out force vs. pull-out distance](image.png)

**Figure 8.9** Variation of pull-out force throughout the pull-out process of CNTs with different curvatures from epoxy matrix as a function of pull-out displacement.

### 8.4.2 Effect of CNT agglomerate size

Five MD simulations of the pull-out test of CNT bundles of different diameters were conducted to determine quantitatively the effect of agglomerate size on the interaction/binding energy, pull-out force, and ISS of CNT-epoxy composites. The respective pull-out test of four bundles consisting of three, seven, nineteen, and thirty-seven CNTs were simulated and the results were compared with the pull-out of a single CNT. The pull-out process was completed until the fully embedded nanotube bundles were completely pulled out from the epoxy. Fig. 8.10 shows snapshots of the pull-out simulation for the five nanocomposite systems considered. The CNT-epoxy binding energy is shown in Fig. 8.11. All CNTs in the modeled bundles were straight which explain the linear relation of the binding energy with the distance moved along the pull-out direction. The results show that the interfacial energy increases with the increase of bundle size.
The interaction energy between the embedded nanotubes and the surrounding polymer chains originates solely from vdW non-bonded interactions. The number of the interactions increases with the increase in the interface area between the outer layer of the bundle and the polymer. The pull-out forces shown in Fig. 8.11 were calculated from the slope of the binding energy curves. The average ISS between the CNT bundles and the epoxy polymers is calculated by dividing the pull-out force by the interface area of the bundle:

\[
ISS = \frac{F_{\text{pull-out}}}{A_{\text{interface}}} = \frac{F_{\text{pull-out}}}{N_{\text{CNTs}} \beta_{\text{bundle}} \pi (D_{\text{CNT}} + h_{vdw}) L_{\text{CNT}}}
\]

(8.7)

Where \(N_{\text{CNTs}}\) is the number of CNTs in the bundle and \(\beta_{\text{bundle}}\) is a parameter that determines the portion of the CNTs in the outer layer in the interface. The surface area was calculated using a similar methodology offered by Peigney et al. [42], in which the surface area of a bundle decreases with the increase of the bundle diameter or number of layers. Table 8.4 summarize the parameters used in the calculation of the interface area and the main output results for agglomerated cases. Figure 8.12 shows the variation of the ISS with the number of CNTs inside the bundle.

\[\text{Figure 8.10} \text{ Snapshots of the nanocomposite system at the middle of the pull-out of: (a) a single CNT, (b) a bundle of three CNTs, (c) a bundle of seven CNTs, (d) a bundle of nineteen CNT and (e) a bundle of thirty-seven CNT.}\]
An approximate function relating the number of CNTs, \( N_{\text{CNT}} \), in the bundle and the ISS is obtained by curve fitting the simulation results:

\[
\text{ISS} = 45.92 \times N_{\text{CNT}}^{-0.116}
\]  

(8.8)

The relationship between the ISS and the number of CNTs in the bundle is non-linear in which the ISS exhibits a rapid initial decrease with the increase of the agglomerate size. This decrease is caused by the substantial reduction in the effective surface area of the bundle compared with the total surface area of a single well-dispersed CNT. Increasing the bundle size further, leads to a relatively slow reduction in the ISS. Well-dispersed CNTs have higher interfacial properties due to their large surface to volume ratio. CNT agglomerates do not enjoy this property, which explains the reason for the observed deterioration in the mechanical properties of CNT-reinforced composites at higher CNT volume fractions [55,56]. These CNT agglomerates act as failure initiation sites due to their poor interfacial adhesion with the surrounding matrix [57,58].
Table 8-4 Parameters used in calculating the ISS and the main output results of the MD study of effect of bundle size.

<table>
<thead>
<tr>
<th>Case #</th>
<th>Number of CNTs in the bundle</th>
<th>$\beta_{bundle}$</th>
<th>Binding energy (Kcal/mole)</th>
<th>$F_{pull-out}$ (nN)</th>
<th>ISS (MPa)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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</tr>
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</tr>
<tr>
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<td>10/37</td>
<td>-8050.2</td>
<td>7</td>
<td>30.9</td>
</tr>
</tbody>
</table>

### 8.4.3 Combined effect of CNT agglomeration and waviness

The results obtained for the separate effect of CNT waviness and agglomeration on the interfacial properties are used here to determine their combined effect on the ISS. All agglomerates are considered to be of hexagonal shapes. An approximate function relating the waviness ratio, $\alpha$, and the number of CNTs in the nanotube bundle, $N_{CNT}$, with the ISS is obtained; as follows:

$$ISS = \gamma \ast ISS^* \quad (8.9)$$

where $ISS^*$ is the interfacial shear stress between straight and well-dispersed (i.e. individual) CNT and epoxy matrix, and $\gamma$ is a parameter that determine the effect of CNT curvature ratio and agglomerate size. The value of the parameter $\gamma$ is obtained by the following equation:

$$\gamma = N_{CNT}^{-0.116} \ast (320.6 \alpha^3 - 162.9 \alpha^2 + 31.4 \alpha + 1) \quad (8.10)$$

Figures 8.13 shows the variation of the ISS with the waviness ratio and the number of the CNTs in the bundle. This Figure can be used to obtain the ISS for CNTs with a wide range of curvatures and agglomerate sizes. It is clear from these result that the presence of CNTs agglomerates cancels any improvement in the ISS and eventually leads to a deterioration in the elastic properties due to the limited stress transfer from the matrix to the embedded nanotubes.
Figure 8.12 Variation of the ISS as a function of the number of CNTs inside the bundle.

**Equation:**

$$\text{ISS} = 45.92 \times N_{\text{CNT}}^{-0.116}$$

Figure 8.13 Variation of the interfacial shear stress with the number of CNT layers and waviness ratio of the CNTs inside the pulled-out bundles.
8.5 Conclusions

In this article, we conducted molecular dynamics simulations to determine the effect of nanotube waviness and agglomeration on the interfacial strength of CNT-reinforced thermoset composites. The effect of waviness was considered by modeling curved nanotube with different curvatures, ranging from straight to highly curved. The effect of CNT agglomeration was considered by modeling nanotube bundles of different sizes. The simulations results were used to develop a generalized relation for the ISS of CNT-epoxy composites that takes into consideration the effect of waviness and agglomeration of CNTs. The results reveal that waviness and agglomeration, which are typical in nanocomposites, play a significant role in determining the interfacial strength of CNT-reinforced thermoset epoxies. Our findings outline some of the causes and sheds light on the large discrepancy that exists in the literature in the interfacial shear strength of nanocomposites. Specifically, our work reveals the following:

(i) the ISS increases with the increase in the waviness ratio of the CNT,

(ii) the force required to initiate the pull-out of a curved CNT was found to be significantly larger than that needed for a straight CNT, and this was determined to be due to the work required to straighten the curved structure,

(iii) the influence of waviness on the interface strength starts to diminish when the CNTs agglomerate into bundles, and

(iv) the ISS decreases significantly with the increase in the size of the CNT bundle.

8.6 Acknowledgements

This work is supported by the Science and Engineering Research Council of Canada and the Discovery Accelerator Supplement.

8.7 References


J. Wernik, PhD, University of Toronto, 2013.


PART III

Modeling of Electromechanical Properties of CNT-Reinforced Polymer Composites

Summary: In the third part, we investigated the percolation, electrical, and piezoresistive properties of CNT-reinforced polymer composites. As this is a non-traditional format paper-based thesis, the below chapter 9 has been written in the form of a journal paper. In it, we coupled the electrical and mechanical properties using a novel multiscale model. The elastic constants of the composite constituents were obtained at the nanoscale using MD simulations. These properties were then used to define the material properties of a RVE representing the nanocomposite. The structural response of the RVE was determined using a 3D FE model and the corresponding electrical response was then obtained using the modified nodal analysis electrical technique.
Chapter 9.
Paper #7: Multiscale Modeling of the Coupled Electromechanical Behavior of Multifunctional Nanocomposites

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As this is a non-traditional format paper-based thesis, this chapter has been written in the form of an article that has been submitted to Physical Chemistry Chemical Physics (PCCP) journal.

9.1 Abstract

In this first time effort we developed a multiscale electromechanical model capable of computing the piezoresistive properties of carbon nanotubes (CNT) reinforced composites. At the atomic scale level, the effective properties of the nanocomposite constituents were determined using molecular dynamics simulations. The obtained elastic moduli of the dispersed CNTs and the surrounding epoxy polymer were used as an input to a coupled electromechanical model. Monte-Carlo based algorithm was used to generate microscale representative volume elements (RVEs) randomly filled with CNTs surrounded by the polymer matrix. Periodic boundary conditions were imposed on the CNTs that cross the boundaries of the RVE. The coupling between the applied mechanical load and the resulting electrical response was treated in a sequential manner in two steps. Firstly, a three-dimensional finite element (FE) model of the RVE was developed to determine the structural response of the nanocomposite system under different loading conditions. The results of the FE model were then used to update the locations of the CNTs in the deformed RVE. Secondly, an electrical model based on the modified nodal analysis technique was developed to calculate the electrical conductivity of the nanocomposite prior to and post the deformed conditions. The developed model was successfully used to determine the piezoresistive behavior of CNT-epoxy composite under tension, compression, and shear loads. The results show that the composite gauge factor can reach up to 3.95 and is sensitive to the loading direction and CNT volume fraction. The predictions of the current model are in good agreement with the experimental findings of earlier studies, verifying its validity.
9.2 Introduction

Because of the one-dimensional nature and defect free structure of CNTs, electrons can move through them ballistically without scattering [1]. They can carry current densities of up to 10^9 A/cm^2 [2]. Dispersing a small fraction of CNTs into an insulating polymer transforms it into an electrically conductive material as a result of the formation of percolating CNT conducting networks. Owing to this remarkable property, CNTs have emerged as one of the most promising reinforcement materials to tailor the multifunctional properties of polymer-based nanocomposites [3]. Furthermore, with the increased use of composite materials in the aerospace industry, more advanced applications for CNT-reinforced composites that require multifunctional properties are being explored. These include, strain sensing, electromagnetic interference shielding of electronics, and lightning strike protection for aerospace vehicles [4,5].

CNT-based sensors have been often considered unsuitable for practical applications due to their unpredictable characteristics [6]. To overcome this problem, polymer adhesives were introduced to prevent the break down of the conductive pathways inside the CNT-based sensor [7]. The electrical current in CNT-reinforced composite films is transmitted through networks of percolating CNT networks spanning through the material and connecting the two sides of the conductive films via ballistic transport of electrons along CNTs (intrinsic resistance) and electron tunneling between sufficiently close CNTs (tunneling resistance) [8–11]. The electromechanical behavior of the nanocomposite is attributed to the change in the intrinsic resistances of the deformed CNTs due to the shift in the G band [12], and the change in the tunneling resistances between adjacent CNTs in percolating networks in response to CNTs dislocations during loading [13]. In order to successfully utilize such nanocomposite in structural health monitoring applications, a number of experimental [14–19], analytical [20–24], and numerical studies [25–27] were conducted over the past decade to study their piezoresistive behavior.

Experimentally, Wichmann et al. [28] developed strain sensor from a MWCNT/epoxy composite that is capable of measuring bending deflection by generating a gradient in electrical conductivity throughout the composite block. Their measurements showed a nearly linear relationship between the sensor resistance and the applied mechanical strain. Böger et al. [29] developed a conductive adhesive from epoxy matrix reinforced with CNTs to monitor the condition of glass fiber reinforced composites subjected to tensile and fatigue loadings. Their results showed that the
developed monitoring method had a higher sensitivity compared to other damage sensing techniques. Thostenson and Chou [30] developed an in situ sensor for damage detection and evolution in advanced fiber composites during cyclic loads by utilizing the piezoresistivity of CNT-based adhesives. The variation of the electrical resistance showed a clear indication of crack opening and closure under cyclic loading.

Park et al. [31] investigated the strain-dependent electrical resistance of polyethylene oxide reinforced with different volume fractions of MWCNTs. The resistance-strain curves consisted of an initial linear region followed by a nonlinear region. The slope and size of each region was found to depend on the CNT volume fraction. Kang et al. [32] managed later to develop a SWCNT/polymide composite with piezoresistive coefficient significantly higher than metallic strain gauges. Experimental results presented by Yasuoka et al. [15] showed that the strain dependent electrical resistance of CNT-reinforced composites decreases nonlinearly with the increase of the CNT concentarion. Oliva-Avilés et al. [33] managed to improve the electrical conductivity and piezoresistive properties significantly by aligning the dispersed CNTs in the composite. The gauge factor of the resulting composite reached 3.2, which is higher than those reported for commercial metal foil gages. More recently, CNTs were successfully incorporated with polyurethane elastomer to develop a new nanocomposite sensor for measuring tensile strains up to 400% [7].

Additionally, a number of analytical models were developed to investigate the electromechanical coupling behavior in in CNT-reinforced composites and adhesives [20,22]. For example, Anand et al. [20] developed a mathematical model based on Bruggeman’s effective medium theory to study the nonlinear electromechanical coupling of CNT-epoxy composite thin films. They attributed the nonlinear strain-dependent resistance behavior to the increase in the effective energy band-gap of the composite due to the relatively large strains in the polymer matrix. Shindo et al. [22] developed an analytical model to predict the resistance change resulted from crack propagation in CNT-reinforced composites. The electrical current was assumed in their model to be transmitted through conductive parallel pathways formed from the percolating CNTs. The change in the conductivity during the fracture was assumed to originate from the loss of the conductive pathways passing through the crack surface.
Furthermore, different numerical schemes were developed over the last decade to overcome the limitations experienced in analytical models [31,34]. For example, Park et al. [31] developed a simplified model to calculate the change in resistance of a CNT-polymer film under tensile load. In their model, the tunneling resistance was only assumed to have an influence on the overall conductivity of the composite at relatively high strains due to the overlapping of CNTs at contact locations. A more advanced model was developed by Li et al. [34] to investigate the mechanism of damage sensing in glass fiber composites reinforced with CNTs. In their two dimensional (2D) electromechanical model, the percolating CNT networks were considered as a pseudo 3D network formed from resistors representing tunneling resistances between the embedded CNTs. The electrical conductivity of the system was obtained using the FE method for electrical circuits, while the structural response of the system was determined using 2D finite element (FE) analysis. The crack onset and propagation were monitored in the FE model by considering a damage model based on the simplified maximum principal tensile stress criterion. The resulting change in the electrical conductivity indicated that damage initiation occurs in the cross-ply. More advanced models were developed later in Refs. [35,36] to study the piezoresistive behavior of CNT reinforced polymers by combining a 3D resistor network model and a fiber reorientation model to update the location of each CNT in the percolating network under different strain levels. The electrical conductivity of the strained RVE was then calculated and the obtained relationship between the resistance and the applied strain was used to calculate the piezoresistive coefficient of the sensor.

However, the attempts to investigate CNT-reinforced composites came short of capturing the complexity of the material structure at the nanoscale level and were not able to consider the interactions between the dispersed CNTs [37]. As a result, the electromechanical coupling mechanisms of CNT-polymer composites remain unclear [34]. In this work, we overcame these inherent limitations by developing a coupled electromechanical multiscale model that utilizes the material properties at the nanoscale to obtain the structural response of 3D FE models at the micro-level using representative volume elements for the nanocomposite under different loads. A search algorithm was then developed to identify the percolating CNT networks and the modified nodal analysis method was then implemented to calculate the effective resistance of the RVE. The output from the FE models was then repeatedly used to update the locations of CNTs inside the
electrical model and to subsequently determine the corresponding electrical response of the nanocomposite.

9.3 Simulation Procedure

The proposed coupled electromechanical multiscale model is developed in three steps, as shown in Fig. 9.1. Firstly, MD simulations are used to determine the transversely isotropic stiffness tensor of a SWCNT and the isotropic stiffness tensor of pure epoxy polymer. Secondly, a Monte Carlo based algorithm is developed to randomly disperse CNTs in a cube (RVE) representing the surrounding polymer matrix. Large-scale 3D FE simulations are performed to determine the structural response of the RVE under compression, tensile, and shear loads. The obtained elastic moduli at the nanoscale level are used to define the material properties in the FE model. Thirdly, an advanced algorithm is developed to identify the percolating CNT networks in the RVE in all directions and transform them into an equivalent electrical circuit formed from tunneling and intrinsic resistances.

![Diagram](image)

**Figure 9.1** Coupling sequence in the proposed electromechanical model: (a) MD model of the composite constituents, (b) hybrid FE-MD model, and (c) percolating CNTs network identified using the developed electrical model.
The polymer matrix is considered in the electrical model as a barrier material that affects the tunneling resistance between adjacent nanotubes. Periodic boundary conditions are imposed in all directions and the electric current was measured along each direction using the modified nodal analysis method. The deformed RVE is incorporated into the electrical model by updating the coordinates of the CNTs in the electrical model and the corresponding electrical response is then determined. The strain gauge factor of the composite is obtained from the relationship between the change in the electrical resistance and the applied strain.

9.4 Electrical Model

Monte-Carlo simulations were used in the present study to determine the percolation probability and the effective electrical conductivity of CNT-epoxy composites by averaging the results of 100 samples per data point. RVEs reinforced with different volume fractions of randomly dispersed SWCNTs were generated with a developed algorithm, as shown in Fig. 9.2 (a). All CNTs were assumed to be straight and well dispersed in the RVE in this investigation. Each CNT can be defined in the electrical model with two points located at its two ends along the axis. The location of the first point of the $i^{th}$ CNT is randomly generated by:

$$X_i^1 = rand \times L_{RVE}, \quad Y_i^1 = rand \times L_{RVE}, \quad Z_i^1 = rand \times L_{RVE}$$  (9.1)

where $rand$ is a uniformly distributed random number in the in the interval $(0,1)$ and $L_{RVE}$ is the side length of the RVE. The orientation of each CNT is also randomly generated and can be defined by the corresponding azimuthal $\varphi_i$ and polar $\theta_i$ angles:

$$\varphi_i = rand \times 2\pi \quad \text{and} \quad \cos(\theta_i) = \cos(\theta_{max}) + rand \times (1 - \cos(\theta_{max}))$$  (9.2)

where $\theta_{max} = \frac{\pi}{2}$ was used to generate uniformly distributed CNTs in all directions ($\theta_{max} = 0$ for aligned CNTs). The location of the second point of the $i^{th}$ CNT can be then obtained by:

$$X_i^2 = X_i^1 + L_{CNT} \cos(\theta_i)$$  (9.3)

$$Y_i^2 = Y_i^1 + L_{CNT} \sin(\theta_i) \cos(\varphi_i)$$  (9.4)

$$Z_i^2 = L_{CNT} \sin(\theta_i) \sin(\varphi_i)$$  (9.5)
where $L_{CNT}$ is the CNT length. Periodic boundary conditions were imposed on the CNTs that cross the boundaries of the RVE, as shown in Figs. 9.2 (b) and 9.2 (c).

![Diagram](image)

**Figure 9.2** Schematic representations of Monte Carlo method: (a) randomly distributed CNT showing the parameters governing its location and orientation, (b) RVE prior to applying periodic boundary conditions and (c) RVE after applying the periodic boundary.

In order to simulate the percolating CNT networks inside the composite, an equivalent electric circuit was developed by modeling the randomly dispersed CNTs as cylindrical rods. The surrounding polymer matrix is considered as a barrier material that affects the tunneling resistance between adjacent CNTs. Figure 9.3 shows a flowchart of the steps taken to develop the appropriate algorithm to identify a percolating network in an RVE. The percolating CNT network was built by checking the existence of continuous paths between any two opposite sides of the RVE (see Fig. 9.4 (a) to 9.4 (c)). The intersection between two rods was assumed to exist if the minimum distance between them was less than the maximum tunneling distance [8,38]. The percolation probability at a specific CNT volume fraction is the number of percolating RVEs over the total number of all RVEs ($N_{per}/N_{total}$) and the percolation threshold $\phi_c$ is the volume fraction at which 50% of the samples percolate.

Once the percolating CNT network is identified, an equivalent resistance network was then developed by transforming the percolating CNT network into an equivalent resistors circuit [13], as shown in Fig. 9.4 (d). Each joint in the percolating network was modelled as a series of equivalent electrical resistance consisting of intrinsic resistance $R_{CNT}$ to model the CNT and
tunneling resistance $R_{contact}$ to model the resistance to electron tunneling between the interacting CNTs; viz.:

$$R_{CNT} = \frac{4L_{CNT}}{\pi \sigma_{CNT} d_{CNT}^2}$$  \hspace{1cm} (9.6)

$$R_{contact} = \frac{h}{2e^2 M T}$$  \hspace{1cm} (9.7)

where $\sigma_{CNT}$ is the intrinsic electrical conductivity of the CNT, $d_{CNT}$ is the CNT diameter, $h$ is Planck’s constant, $e$ is the electron charge, and $M$ is the total number of conduction channels [39–41].

---

**Figure 9.3** The algorithm used to identify the percolating networks in the developed electrical model. The input parameters to this simulation step are CNT length, diameter, RVE size, and number of samples.
Figure 9.4 Sequence adopted in building the equivalent electrical circuit: (a) dispersing the required number of CNTs inside the RVE, (b) transforming all CNTs into 3D line segments, (c) backbone of the percolating network that enables the current to be transmitted, and (d) equivalent electric circuit of the percolating network.

The transmission probability $T$ can be calculated by solving the Schrödinger equation for rectangular potential barrier:

$$T = \exp \left( - \frac{d_{min} - d_{CNT}}{d_{tunnel}} \right) \quad h_{vdW} \leq d_{min} \leq d_{cut-off}$$

(9.8)

Where $d_{min}$ is the thickness of the polymer layer between the two CNTs, $h_{vdW}$ is the van der Waals separation distance, $d_{cut-off}$ is the cutoff distance, and $d_{tunnel}$ is the tunneling characteristic length. Further discussion of the influence of the tunneling resistance on the overall electrical properties of the nanocomposite can be found in our previous papers [8,42,43].

A matrix is then created for each resistor element in the percolating network; as follows:
\[
\begin{align*}
\{I^n\} \{v^n\} = [K_{ij}]^e \{v^n\} = \frac{1}{R^e} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \{v^n\}
\end{align*}
\]  

(9.9)

where \(i\) and \(j\) refer to the end nodes of the resistor, \(I_i^e\) is the electric current passing through this node, \(v_i\) is the nodal voltage, \(K_{ij}^e\) is the element conductance, and \(R^e\) is the element resistance. The local matrices for all resistors are then assembled to build the resistor matrix for the entire percolating network, \(K\), according to Kirchhoff’s current law [44]:

\[
K = \sum_{e=1}^{m} [K_{ij}^e]
\]

(9.10)

where \(m\) is the total number of resistances in the percolating network. The effective resistance of the percolating networks is then obtained using the modified nodal analysis (MNA) method as follow:

\[
\begin{bmatrix} I_{\text{external}} \\
V_{\text{source}} \end{bmatrix} = \begin{bmatrix} K & -1 \\ +1 & 0 \end{bmatrix} \begin{bmatrix} V_{\text{nodal}} \\
I_{\text{source}} \end{bmatrix}
\]

(9.11)

where, \(I_{\text{external}}\) is the external current which is zero in our case, \(V_{\text{source}}\) is the voltage between the two opposite ends of the RVE (points 0 and 1 as shown in Fig. 9.4 (d)), \(V_{\text{nodal}}\) is the nodal voltages, and \(I_{\text{source}}\) is the electric current that pass through the circuit due to the applied voltage [45]. The equivalent resistance of the circuit is then obtained using Ohm's law:

\[
R_{\text{effective}} = \frac{V_{\text{source}}}{I_{\text{source}}}
\]

(9.12)

### 9.5 Coupled Electromechanical Model

Several RVEs reinforced by randomly dispersed CNTs with volume fractions ranging from 0.1% to 0.3% were constructed by modeling CNTs as solid cylinders that are fully coupled to the surrounding polymer. A hybrid FE model was developed to determine the structural response of each RVE subjected to uniaxial tensile, uniaxial compression, volumetric tension, volumetric compression, and shear loads applied independently. Figure 9.5 shows the constructed 3D FE models of RVEs with aspect ratio \(L_{\text{RVE}}/L_{\text{CNT}}\) equals 1 and all nanotubes are selected to be \((5,5)\) armchair SWCNT of length 68 Å and aspect ratio \(L_{\text{CNT}}/d_{\text{CNT}}\) ~100. All FE models were modeled with quadratic tetrahedral elements and the material of the CNT and the matrix were both assumed
to be homogeneous and isotopic. Furthermore, the material properties of both the CNTs and the epoxy polymer were assumed to be linear elastic with elastic moduli defined from the initial slope of the stress-strain curves of the atomistic models. Table 9.1 summarizes the of the constructed FE models for this investigation.

The structural response of each RVE was obtained by applying incremental strains up to 10% total strain. The locations of the CNTs in the deformed RVEs are then obtained and used as an input to the electrical model to update their positions and the corresponding CNTs’ percolating networks. The intrinsic and tunneling resistances were then recalculated for the strained RVE and the effective electrical resistance of the composite was calculated using the developed electrical-circuit code. The strain gauge factor (GF) of the CNT-epoxy sensors is then obtained from the relationship between the change in the RVE resistance and the applied strain; viz:

\[
GF = \frac{(\Delta R / R_0)}{(\Delta L_{RVE} / L_{RVE})} = \frac{(\Delta R / R_0)}{\varepsilon}
\]  

(9.13)

where \( R_0 \) and \( \Delta R \) are the initial resistance and the change in the resistance of the RVE, respectively. \( L_{RVE} \) and \( \Delta L_{RVE} \) are the initial length and the change in the length of the RVE, respectively.

**Table 9-1** Data of all finite element models used in investigating the electromechanical coupling of CNT-reinforced composites. All RVEs have an aspect ratio of 1 and all CNTs are (5,5) SWCNT with aspect ratio 100.

<table>
<thead>
<tr>
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<th>CNT vol. %</th>
<th>Total Number CNTs</th>
<th>Total Number line segments</th>
<th>Total Number of nodes</th>
<th>Total Number of elements</th>
<th>Initial conductivity (S/m)</th>
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<td>311240</td>
<td>204105</td>
<td>0.2009</td>
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<tr>
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<td>26</td>
<td>56</td>
<td>731715</td>
<td>499809</td>
<td>0.6321</td>
</tr>
<tr>
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<td>39</td>
<td>82</td>
<td>997495</td>
<td>706080</td>
<td>1.143</td>
</tr>
</tbody>
</table>
Figure 9.5 Finite element models representing cubic RVEs, with side length of 68 nm reinforced with (a) 0.1 vol. %, (b) 0.2 vol. %, and 0.3 vol. % of CNTs. All models are meshed with quadratic tetrahedral elements.
9.6 Results and discussion

9.6.1 Percolating and Conducting Networks

In this section, we will present the obtained results from the developed electrical Monte Carlo model for CNT-reinforced polymer composites. All CNTs were randomly dispersed inside the RVEs where the minimum distance between any two CNTs were set to be greater than $(d_{CNT} + h_{vdW})$, where $h_{vdW}$ is the van der Waals separation distance. $h_{vdW}$ was set to be 3.4 Å, which is the inter-tube separation distance in multi-walled CNTs [46]. The intrinsic conductivity $\sigma_{CNT}$ was set to $1 \times 10^4$ for both SWCNTs and MWCNTs [47,48]. The maximum tunneling distance was set to be 1.4 nm and the barrier height between the CNT and the surrounding epoxy was set to be 1 eV [49]. First, the proper size of the RVE was investigated by considering aspect ratios $(AR_{RVE}=L_{RVE}/L_{CNT})$ ranging from 0.75 to 1.5. In the size investigation, RVE reinforced with MWCNTs of 50 nm diameter and 5 µm length were considered. All CNTs were randomly dispersed in the RVE ($\theta_{max} = 90^\circ$). Periodic boundary conditions were imposed on all CNTs crossing the RVE boundaries to reduce the size effect. Figure 9.6 (a) and 9.6 (b) show the variation of the electrical and percolation probability of the nanocomposite with the CNT volume fraction for different RVE sizes, respectively. Each point in these curves is the average value of 100 simulations.

At lower volume fractions near the percolating threshold, the electrical conductivity increases with the decrease of the RVE size. However, this difference diminishes at higher CNT volume fractions. On the other hand, the percolation threshold converged to an almost single value (50% of the samples percolated at ~0.25 vol.% of CNTs) depicting its independence of the RVE sizes considered in this work, as shown in Fig. 9.7. The results show that the applied periodic boundary conditions reduced the effect of RVE size on the electrical and percolating properties.
Figure 9.6 The influence of RVE size on (a) the electrical and (b) percolation properties of CNT-reinforced composites obtained with Monte Carlo simulations and modified nodal analysis technique.
The electrical conductivity predicted by the developed percolation and electrical algorithm in this study was then validated by comparing its results with those obtained experimentally in the literature for MWCNT-reinforced polymer composites [49,50]. Based on the RVE size investigation, RVE with aspect ratio equal 1 was selected for the comparison investigation. Figure 9.7 shows the variation of the electrical conductivity with CNT concentration up to 5%. The obtained results show that the electrical conductivity follows the percolation theory with a percolation threshold in the range 0.2-0.5 vol.%, where the electrical conductivity suddenly increases by several orders of magnitude due to the formation of increased percolating paths through the material. The electrical conductivity kept increasing with increasing the CNT concentration and reached up to 100 S/m at 5.0 vol.%. The obtained results showed a good agreement with those obtained experimentally.

![Figure 9.7 Comparison of predicted electrical conductivity with existing experimental data [49,50].](image-url)
9.6.2 Electromechanical Response

After verifying the ability of the developed electrical model to identify the percolating CNT networks and calculating their effective electrical resistance, this model was coupled with a mechanical model to predict the effect of CNT volume fraction and loading direction on the piezoresistive properties of CNT-reinforced epoxy composites. Three FE models were constructed to model nanocomposites reinforced with 0.1 vol. %, 0.2 vol. %, and 0.3 vol. % of CNTs. These near percolation threshold volume fractions were selected because the electrical response of the nanocomposite at such concentration has a relatively high sensitivity to the applied deformation [51]. Based on the RVE size investigation, the RVE aspect ratio for the electromechanical investigation was selected to be 1, which was also proven in our previous work [52] to be able to capture the mechanical properties of the composite. All CNTs were considered to be fully bonded to the surrounding polymer matrix. To model the surrounding matrix, we used a specific two-component epoxy material based on a diglycidyl ether of bisphenol A (DGEBA) epoxy resin and triethylene tetramine (TETA) curing agent, which is typically used in the aerospace industry [52]. Armchair (5, 5) CNTs with an aspect ratio of 100 were used in this investigation as the reinforcement material. The properties of the nanocomposite constituents were taken from our previous MD studies [53,54] (see Table 9.2).

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure epoxy polymer [53]</td>
<td>3.2</td>
<td>0.39</td>
</tr>
<tr>
<td>(5,5) armchair SWCNT [54]</td>
<td>860</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The first FE model (see Fig. 9.5 (a)) represents a nanocomposite reinforced with 0.1 vol.% of CNTs was subjected to different five boundary conditions to determine the piezoresistive behavior of the material to each load. Uniaxial tensile along x-direction ($\varepsilon_{xx} = 10\%$), uniaxial compression along x-direction ($\varepsilon_{xx} = -10\%$), volumetric tension ($\varepsilon_v = (1 + \varepsilon_{xx})(1 + \varepsilon_{yy})(1 + \varepsilon_{zz}) - 1 = 10\%$), volumetric compression ($\varepsilon_v = (1 + \varepsilon_{xx})(1 + \varepsilon_{yy})(1 + \varepsilon_{zz}) - 1 = -10\%$), and shear strain ($\varepsilon_{xy} = 10\% (\alpha = 5.7^\circ)$) deformations were applied to this FE model to identify the
unique material response to each deformation. The obtained results will help designing a new sensor that is able to determine the type and magnitude of the load.

Figure 9.8 (a) and 9.8 (b) shows FE model for case 1 before and after applying 10% uniaxial tensile strain in x-direction, respectively. The positions of the CNTs in the deformed FE model were mapped into the electrical model for each strain increment to find the corresponding percolating network, as shown in Fig. 9.8 (c) and 9.8 (d). The intrinsic and tunneling resistances were then recalculated for the strained RVE and the effective electrical resistance of the composite was calculated using the developed electrical-circuit code.

![Figure 9.8](image)

(a) Undeformed FE model                   (b) Uniaxially tensile ($\varepsilon_x = 20\%$)

(c) Initial percolating network           (d) deformed percolating network

**Figure 9.8** Snapshots of the FE model for case # 1 (Vol 0.1%) (a) before and (b) after applying a uniaxial tensile strain of 10% along x-direction. CNTs percolating network along x-direction identified using the developed electrical model for (c) initial and (d) deformed RVE.
Figure 9.9 shows a close-up view of two CNTs in contact before and after the breakdown ($d_{\text{min}}>1.4$ nm) of the percolating network due to the applied strain. The corresponding change in the electrical conductivity and change in effective resistance over the initial resistance ($\Delta R/R_0$) of the RVE under different loading conditions are shown in Fig. 9.10 (a) and 9.10 (b), respectively. These results show that the electric properties of the nanocomposite change linearly with the applied strain up to 3.0% strain. At higher strains, the electrical properties start to fluctuate. However, the general trend of the curves continued in the same direction. These fluctuations are caused by the large deformations induced in the FE model and the inability of the electrical model to account for any bending (induced curvature) in the CNTs that occurs at higher strains (see Fig. 9.8 (b)). It is very clear that the electromechanical behavior is strongly dependent on the direction and type of the strain. We calculated the strain gauge factor (GF) from the slope of the change in resistance over the initial resistance with the applied strain. The obtained GF varies from 1.53 for shear deformation to 3.95 for volumetric tension. Table 9.3 summarizes the results for all loading conditions.

![Figure 9.9](image)

**Figure 9.9** The finite element model used to determine the structural response. (b) A close view of one of the contacts between adjacent CNTs before (closed percolating path) and after (open path) applying an external load.
Figure 9.10 The variation of (a) the electrical conductivity and (b) the change in electrical resistance over the initial resistance ($\Delta R/R_0$) of the RVE for case #1 (0.1 vol.%) with the applied strain for different loading conditions.
Table 9-3 strain gauge factors (piezoresistivity coefficient) for case #1 (epoxy polymer reinforced with 0.1 vol.% of SWCNTs) for different loading conditions obtained using the developed electromechanical model.

<table>
<thead>
<tr>
<th>Vol. %</th>
<th>Case #</th>
<th>Gauge factor (GF) or piezoresistivity coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uniaxial tension</td>
</tr>
<tr>
<td>0.1</td>
<td>1</td>
<td>-2.77</td>
</tr>
</tbody>
</table>

We extended our investigation to consider the effect of CNT volume fraction on the electromechanical coupling of nanocomposite considered. Three FE models were constructed to model an epoxy polymer reinforced with 0.1%, 0.2% and 0.3% volume fractions of CNTs, which corresponds to the formation of single, double, and triple percolating paths inside the RVEs, respectively, as shown in Fig. 9.11. All FE models were subjected to both uniaxial tensile and compressive loads and the obtained deformations were used to update the electrical models in each case. The gauge factor for all cases was then obtained from the slope of the resistance with the applied strain. Table 9.4 summarizes the results for all cases. The obtained results show that the gauge factor for the nanocomposite drops when the CNT concentration becomes higher than the percolation threshold. This could be attributed to the formation of an increasing number of percolating networks that spreads in all directions throughout the composite, which makes the material less sensitive to the applied load. The obtained results from the developed electromechanical model are in a good agreement with those obtained experimentally by Oliva-Avilés et al. [33], where they managed to manufacture nanocomposite films with gauge factor up to 3.2.

Table 9-4 strain gauge factors predicted for RVEs with different volume fractions under uniaxial tensile and compression loading conditions.

<table>
<thead>
<tr>
<th>Vol. %</th>
<th>Case #</th>
<th>Gauge factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uniaxial tension</td>
</tr>
<tr>
<td>0.1</td>
<td>1</td>
<td>-2.77</td>
</tr>
<tr>
<td>0.2</td>
<td>2</td>
<td>-0.63</td>
</tr>
<tr>
<td>0.3</td>
<td>3</td>
<td>-0.98</td>
</tr>
</tbody>
</table>
Figure 9.11 CNTs percolating networks along x-direction identified using the developed electrical model for RVEs reinforced with (a) 0.1%, (b) 0.2% and (d) 0.3% volume fractions of CNTs.

9.7 Conclusions

In this first effort, we offer a new coupled electromechanical multiscale model that is capable of determining the piezoresistive behavior of CNT-reinforced composites. The effective properties of the nanocomposite constituents were determined using MD simulations. The obtained elastic constants of the transversely isotropic CNTs and the isotropic polymer matrix at the nanoscale were used as inputs to a coupled electromechanical model. The Monte-Carlo que was used to generate RVEs randomly filled with CNTs. Periodic boundary conditions were imposed on the CNTs that cross the boundaries of the RVE. The coupling between the applied mechanical load and the resulting electrical response was achieved in two sequential steps. Firstly, a 3D FE model of the RVE was constructed to determine the structural response of the nanocomposite system under tension, compression, and shear loads. The displacements of the CNTs in the strained FE model were then updated in an equivalent electrical model of the percolating CNTs network to calculate the corresponding conductivity. The following is a summary of our findings:

(i) the predictions of the electrical, mechanical, and electromechanical models are in good agreement with experimental findings of earlier studies, verifying its validity and reliability,

(ii) the predicted strain gauge factor can be as high as 3.95, which is almost twice the value of common commercial metallic strain gauges,
(iii) the piezoresistive response of the nanocomposite was distinct for the varied shear, tensile, and compressive loads applied; and

(iv) the results of this work can be used in designing a universal strain measuring tool for real-time SHM applications.

In this work, we assumed full bonding between the dispersed CNTs and the host matrix. This indicates that our results represent an upper bound. It is highly recommended to account for agglomeration, waviness, and interfacial debonding of CNTs in future models as well as to consider the effect of combined and complex loading conditions on the constitutive laws governing the electromechanical behavior of the nanostructured composite. Nevertheless, we feel this first effort sets the foundation for future research in this important area.

9.8 Acknowledgment

The authors wish to thank NSERC (RGPIN 42073-13) and the Discovery Accelerator Supplement (RGPAS 446202-13) for their kind support of this research.

9.9 References


M. Wichmann, MSc Thesis, Rice University, 2011.


Chapter 10. Conclusions, Contributions and Future Work

Summary: This chapter provides an overall summary of the conclusions and outlines the original contributions of the work conducted in this thesis. Additionally, we discuss the limitations and assumptions of the accomplished work and provide a brief description of the key areas that would benefit from a follow-up research. The conclusions are divided as per the main headings of the chapters. For detailed conclusions, please review the corresponding work as outlined in the different chapters (published papers).

10.1 Summary of Findings

This thesis consists of two major components: (i) determine interfacial, elastic, electrical, and piezoresistive properties of CNT-reinforced composites for pristine and polycrystalline CNTs using atomistic modeling simulations and (ii) develop a multiscale model that couples electrical and mechanical behaviors at nanoscale and bulk levels.

10.1.1 Atomistic Modeling of the Interfacial Properties

A comprehensive MD study was conducted to determine the effect of CNT dimensions, dispersion state and morphology, and interface thickness on the interfacial properties of CNT-reinforced polymer composites. The change in the interatomic potential during the pull-out simulation was monitored and used to calculate the pull-out force and the ISS between the emended CNTs and the surrounding epoxy matrix. The effect of CNT waviness was considered by modeling nanotubes with a wide range of curvatures ranging from straight to severely curved. The effect of CNT agglomeration was considered by modeling nanotube bundles with different sizes up to 37 CNTs. The results of the pull-out simulations were used to develop a generalized relation for the ISS that takes into consideration the effects of CNT morphology and dispersion state. Specifically, our work reveals the following:

(i) the force required to initiate the pull-out of a curved CNT was found to be significantly larger than that needed for a straight CNT due to the work required to straighten the curved structure,
(ii) the ISS increases with the increase in the waviness ratio of the CNT,

(iii) the influence of waviness on the interface strength starts to diminish when the CNTs agglomerate into bundles, and

(iv) the ISS decreases significantly with the increase in the bundle diameter (i.e. number of hexagonal CNT layers).

10.1.2 Multiscale Modeling of the Mechanical Properties

A multiscale model was developed to determine the effect of nanotube waviness, agglomeration, and alignment on the bulk elastic moduli of CNT-reinforced epoxy composites. Two aspects of the work were examined. First, MD simulations were carried out to determine the orthotropic elastic constants of nanoscale RVEs containing either an individual CNT or agglomerated CNTs embedded in an epoxy matrix. The effect of CNT waviness was also considered by modeling wavy CNTs in the constructed RVEs. Second, the predicted properties from the atomistic simulations were then used as an input to the Mori-Tanaka micromechanical model to determine the bulk elastic properties of nanocomposites reinforced with CNT volume fractions up to 5%. Both aligned and randomly dispersed CNTs were considered in the micro-level analysis to investigate their impact on bulk properties. The developed multiscale model was validated by comparing its results with available experimental data in the literature. The following is a summary of our findings:

(i) the effective elastic properties of the nanocomposite decrease significantly with the presence of CNT agglomerates due to the weak stress transfer inside the nanotube bundles and from these bundles to the surrounding matrix. In addition, these properties also decrease with the increase of the CNT agglomerate size,

(ii) the effective elastic properties of the nanocomposite decrease significantly with increasing the waviness of the reinforcing CNTs, and stabilize after reaching their minimum values at a certain shape factor \( \alpha \),

(iii) the combined effect of agglomeration and waviness results in a significant reduction in the bulk properties of the nanocomposite, and
(iv) the alignment of CNTs improves the effective axial Young’s modulus of the nanocomposite along the alignment direction but reduces the transverse elastic and shear moduli of the nanocomposite.

10.1.3 Large scale MD simulation of RVEs with Realistic Microstructures

Unfortunately, current multiscale modeling techniques are not able to model the interactions between the reinforcing CNTs due to the dilute concentration assumption in micromechanical models. This problem was overcome in this study by modeling large (up to one million atoms) RVEs reinforced by CNTs with aspect ratios up to 500 to simulate nanocomposites with realistic microstructures. A series of MD simulations were conducted to determine the elastic moduli of the nanocomposite using the constant-strain energy minimization method. The following is a summary of our findings:

(i) the proper selection of the RVE size is critical in obtaining reliable results as MD unit cells with side length lower than 1.25 the length of the embedded CNTs were found to overestimate the elastic moduli of the nanocomposite by 25%,

(ii) the stiffness constants of the nanocomposite increase linearly with the increase of the CNT volume fraction; the magnitude of the elastic modulus almost doubles at 5 vol.% of CNTs,

(iii) the dispersed CNTs starts to deteriorate the properties of the polymer when they agglomerate in bundles with diameters over 100 times the diameter of an individual CNT, and

(iv) modeling of RVEs reinforced solely by straight CNTs results in overestimation of the elastic properties.

10.1.4 Influence of grains boundaries on mechanical and fracture properties of CNTs

A systematic and comprehensive MD study was performed to determine the mechanical and fracture properties of polycrystalline CNTs subjected to uniaxial tensile loads. An algorithm based on the Voronoi tessellation method was developed to generate the atomic structures of CNTs of
different diameters that contain a variety of GB types and orientations. The following is a summary of our findings:

(i) contrary to existing studies of polycrystalline graphene, we found that the mechanical performance of CNTs is largely governed by the orientations of GBs but not by the size of the grains,

(ii) CNTs with GBs perpendicular to the tube axis experience a \( \sim 60\% \) strength reduction,

(iii) GBs that are aligned with the CNT axis were found to be less detrimental to the mechanical properties,

(iv) a trade-off exists between the values of Young’s modulus and the fracture strength in cases of random and transverse GBs,

(v) the properties of polycrystalline CNTs depend significantly on the nanotube diameter and temperature, and

(vi) CNTs with specific types of GBs can be optimally engineered and used to tailor the properties of functional devices.

10.1.5 Coupled Electromechanical Modeling of Piezoresistive Properties

A novel coupled multiscale electromechanical model was developed to determine the piezoresistive behavior of CNT reinforced composites. The effective properties of the nanocomposite constituents were determined using MD simulations. The obtained elastic constants of the CNTs and the polymer matrix were used as an input to a coupled electromechanical model. The Monte-Carlo technique was used to generate large scale RVEs randomly filled with CNTs and periodic boundary conditions were imposed on the CNTs that cross the RVE boundaries. The coupling between the applied mechanical load and the resulting electrical response was achieved sequentially in two steps. First, a 3D FE model of the RVE was constructed to determine the structural response of the nanocomposite system under tension, compression, and shear loads. Second, the displacements of the CNTs in the strained FE model were updated in an equivalent electrical model of the percolating CNTs network to calculate the corresponding conductivity. The following is a summary of our findings:
(i) the predictions of the electrical, mechanical, and electromechanical models are in good agreement with experimental findings of earlier studies, verifying its validity and reliability,

(ii) the predicted strain gauge factor can be as high as 3.95, which is almost twice the value of common commercial metallic strain gauges,

(iii) the piezoresistive response of the nanocomposite was distinct for the varied shear, tensile, and compressive loads applied; and

(iv) the results of this work can be used in designing a universal strain measuring tool for real-time SHM applications.

10.2 Thesis original contributions

1. Agglomerated and wavy CNTs were modeled for the first time with atomistic simulations to determine the ISS and elastic constants of CNT-reinforced composites of actual morphologies as imaged with AFM and SEM techniques.

2. The effect of dispersion state, morphology, and alignment of CNTs on the bulk properties of CNT-reinforced polymer composites were successfully determined by scaling up the obtained nanoscale properties to the microscale using both the Mori-Tanaka micromechanical technique and 3D FE models.

3. The unrealistic predictions in nanocomposite properties due to the dilute concentration assumption in micromechanical techniques were overcome in this work by developing the first large scale MD simulations of RVEs representing nanocomposites reinforced with CNT with aspect ratios up to 500, different agglomerate diameters, and a wide range of curvatures. The developed one million atoms systems successfully captured the actual properties of composites systems and can be integrated with electrical and thermal models to predict the multifunctional properties of CNT-reinforced composites.

4. The influence of nanotube curvature, grains size, GB orientations, misorientation angle, and temperature on the elastic and fracture properties of polycrystalline graphene were investigated for the first time in this study via systematic and comprehensive MD simulations.
5. The Monte-Carlo technique was utilized to generate large number of RVEs filled with CNTs. Equivalent electrical circuits were then developed for the percolating CNTs network and the modified nodal analysis method was used to calculate the effective electrical and percolation properties.

6. The first coupled multiscale electromechanical model was developed to study the piezoresistive properties of CNT reinforced polymer composites. The elastic constants of the composite constituents obtained via MD simulation were used as an input to a 3D FE model of a large RVE of randomly dispersed CNTs inside a polymer matrix. The displacements of the CNTs under different loads were obtained from the FE model and used to update the equivalent electrical circuits of the system. The corresponding electrical resistance was then calculated and used to determine the strain gauge factor of the material.

### 10.3 Future work

Given below is a proposed summary of future work that can be conducted in this field. Specifically, the work will benefit from the following considering:

1. The effect of temperature upon the mechanical, interfacial and electromechanical behavior of thermoset and thermoplastic nanocomposites.

2. The effect of defects and damage of CNTs upon the percolated networks of multifunctional nanocomposites.

3. The electrical model used to describe tunneling resistance should be carefully examined and validated experimentally.

4. The work could be extended to treat fiber reinforced composites containing carbon nanotubes.

5. The current research would also benefit from considering the effect of aging upon the mechanical, interfacial and electromechanical behavior of the nanocomposite.

6. The work could be extended to validate the predicted atomistic mechanical and interfacial properties of a single nanotube surrounded by a polymeric material and the corresponding bulk properties experimentally.
Appendix 1: Basics of MD simulations

MD allows us to study relatively large molecular systems that cannot be modeled using quantum mechanics-based techniques such as DFT and ab initio due to the enormous computational cost [2]. The main purpose of MD simulations is to simulate the time dependent behavior of the system by calculating the current and future position and velocity of each atom using Newton's equations of motion. This information can be used later to calculate the averaged mechanical, physical, and thermal properties of the system [3]. The initial position and velocity of each atom in the system must be known at the beginning of the MD simulation. This initial data is randomly generated based on the targeted average temperature of the system using statistical mechanics. The trajectories of the atoms are then determined by solving the Newton's equations of motion of the interacting atoms of the system:

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

(A1.1)

where \( \vec{F}_i \), \( m_i \), and \( \vec{a}_i \) are the acting force, the mass, the acceleration of the \( i^{th} \) atom, respectively. The interatomic force is the gradient of the total potential energy, \( V \), of the system:

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

(A1.2)

The velocity, \( \vec{v}_i \), and displacement vector, \( \vec{r}_i \), of each atom are the first and second derivatives of the acceleration:

\[ \vec{a}_i = \frac{d\vec{v}_i}{dt} \quad \text{and} \quad \vec{v}_i = \frac{d\vec{r}_i}{dt} \]  

(A1.3)

Using Eqs. (A1.1) and (A1.3), the following differential equation can be obtained:

\[ -\nabla V(\vec{r}) = m_i \frac{d^2\vec{r}_i}{dt^2} \]  

(A1.4)

The most popular algorithm to integrate the resulting equations of motion of the system is the Verlet algorithm [4]. In this algorithm, Newton's equations of motion are approximated by a Taylor series expansion:
Adding the above two equations and moving the \( r(t - \delta t) \) term to the right-hand side, we obtain:

\[
r(t + \delta t) = 2r(t) - r(t - \delta t) + a(t) \delta t^2 + O(\delta t^4)
\]  

(A1.7)

This is the general form of the Verlet algorithm for MD simulations, where \( \delta t \) is the time step of the analysis. The truncation error for the position decreases significantly with the decrease in the time step. The value of \( a(t) \) is determined from Eq. (A1.4). Here, we use the positions from the previous and current time steps and acceleration of the current step to predict the trajectory of the atom. The instantaneous velocity \( v(t) \) of each atom can be calculated using Taylor series expansion, as follows:

\[
v(t) = \frac{r(t+\delta t) - r(t-\delta t)}{2\delta t} + O(\delta t^3)
\]  

(A1.8)

The accuracy of the velocity is a function of \( \delta t^3 \) has a lower accuracy than the position which is a function of \( \delta t^4 \). The kinetic energy \( K(t) \) and the averaged instantaneous temperature \( T \) of the system can be calculated using the obtained velocities based on the equipartition theory:

\[
K(t) = \frac{1}{2} \sum_i m_i (v_i(t))^2
\]  

(A1.9)

\[
T(t) = \frac{2}{3} \frac{K(t)}{N \kappa_B}
\]  

(A1.10)

where, \( \kappa_B \) is Boltzmann constant. The averaged stress tensor of the MD unit cell is defined in the form of virial stress [5]; as follows

\[
\sigma = \frac{1}{V} \sum_{i=1}^{N} \left( \frac{m_i}{2} v_i^2 + F_i \cdot r_i \right)
\]  

(A1.11)

where \( V \) is the volume of the MD unit cell.
Potential Function Description

Interatomic potential is a mathematical formulation for calculating the potential energy of interacting atoms at given positions in space [6,7]. Potential functions are empirical in nature with parameters obtained experimentally using X-ray and electron diffraction or numerically using ab initio or semi-empirical quantum mechanics calculations [7,8]. The general expression for the total potential energy of an MD system can be approximated by a many body expansion that depends on the position of three atoms or more [6]:

\[ V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_i^N V_1(\vec{r}_i) + \sum_{i,j}^N V_2(\vec{r}_i, \vec{r}_j) + \sum_{i,j,k}^N V_3(\vec{r}_i, \vec{r}_j, \vec{r}_{ik}) + \cdots \]  

(A1.12)

where \( V_1 \) is the one-body term representing the energy of an isolated atom \( i \) due to an external force field such as the electrostatic force, \( V_2 \) is the two-body term representing the pair-wise interactions of the atoms \( i \) and \( j \) such as Lennard-Jones potential [9], \( V_3 \) is the three-body term representing the three-body interactions and usually called many body interactions such as Tersoff and Brenner potentials, \( N \) is the number of atoms in the system, and \( \vec{r}_i \) is the position vector of atom \( i \) [10,11]. Figure A1.1 shows schematic representations of the interatomic potential energies.

![Interatomic interactions in atomic structures](image)

**Figure A1.1** Interatomic interactions in atomic structures.

In this study, two different interatomic potentials were used in investigating the mechanical properties of CNT-reinforced composites. CVFF force field has been successfully used to predict the elastic properties of CNT-epoxy composites, while AIREBO potential has been used to model CNT-polyethylene composites.
CVFF is a generalized valence force field [12] developed in 1988 by Dinur, and Hagler [12] to simulate over 20 atom types and wide range of materials including protein, water, amino acids, hydrocarbons and other organic molecules, and crystals and gas phase structures [13–15]. The total potential energy in CVFF potential is the summation of bonded interactions and non-bonded interactions. The bonded interactions are divided into diagonal and off-diagonal terms/cross-terms of the valence force field [16]. The diagonal terms represent the energy of deformation/oscillations of bond lengths, bond angles/bending, torsion angles, and out-of-plane interactions. The off-diagonal terms are important to accurately predict the dynamic properties by representing the couplings between deformations of internal coordinates [16]. The nonbonded interactions are represented with van der Waals interactions in the form of a Lennard–Jones function and electrostatic interactions in the form of Coulombic forces [13].

\[
E_{bonded} = \sum_r D_r \left(1 - e^{-a(r-r_0)^2}\right) + \sum_\theta k_\theta (\theta - \theta_0) + \sum_\phi k_\phi \left[1 + \cos(n\phi + \phi_0)\right] + \\
\sum_\chi k_\chi \left[1 + \cos(n\chi + \chi_0)\right] + E_{cross-terms} + \sum_{i>j} \underbrace{\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}}_{\text{van der Waals}} + \sum_{i>j} \underbrace{\frac{q_i q_j}{r_{ij}^{12}}}_{\text{electrostatic}} \tag{A1.13}
\]

Unlike CVFF, AIREBO potential is capable of capturing the interaction between carbon atoms as well as bond breaking and reforming [17]. The AIREBO potential consists of three sub-potentials: the reactive empirical bond order (REBO) potential which calculates the stored energy in atomic bonds, the torsional potential which includes the energy due to torsional interactions between atoms, and the van der Waals in the form Lennard-Jones potential to account for the nonbonded interactions [18]. The stored energy in the bond between atoms i and j can be expressed as:

\[
E_{potential} = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ E_{ij}^{REBO} + \sum_{k \neq i} \sum_{l \neq j, k} E_{ijkl}^{TORSION} + E_{ij}^{LJ} \right] \tag{A1.14}
\]

\[
E_{ij}^{REBO} = f(r_{ij}) \left[ V_{ij}^R + b_{ij} V_{ij}^A \right] \tag{A1.15}
\]

where \(V_{ij}^R\) and \(V_{ij}^A\) are the repulsive and the attractive potentials, respectively; \(b_{ij}\) is the bond order term, which modifies \(V_{ij}^A\) according to the local bonding environment; \(r_{ij}\) is the distance between the atoms \(i\) and \(j\); and \(f(r_{ij})\) is the cut-off function, which limits the interatomic interactions to the nearest neighbours.
Cut-off distance

The purpose of the cut-off function in AIREBO and TERSOFF potentials is to limit the bonded interactions to the nearest neighbouring atom (first-neighbour shell) [11], as shown in Fig. 2a. Selecting the appropriate cut-off function parameters is very critical in obtaining reliable results and avoiding unrealistic hardening behavior observed at higher strains near fracture point [19–21]. The original cut-off function $f(r_{ij})$ of REBO potential component in the AIREBO potential considers a gradual reduction in the interaction between atoms as follows:

$$f(r_{ij}) = \begin{cases} 1 + \cos \left[ \frac{\pi (r_{ij} - R^{(1)})}{R^{(2)} - R^{(1)}} \right] / 2 & r_{ij} < R^{(1)} \\ 0 & R^{(1)} < r_{ij} < R^{(2)} \\ R^{(2)} < r_{ij} & \end{cases}$$ \hspace{1cm} (A1.16)

where $R^{(1)}$ is the inner cut-off radius and is equal to 1.7 Å and $R^{(2)}$ is the outer cut-off radius and is equal to 2 Å, as shown in Fig. A1.2. In order to eliminate the strain hardening near fracture, we considered $R^{(1)}$ to be equal to $R^{(2)}$ which yields a modified cut-off function in the form of a step function:

$$f(r_{ij}) = \begin{cases} 1 & r_{ij} < R \\ 0 & r_{ij} > R \end{cases}$$ \hspace{1cm} (A1.17)

where $R = R^{(1)} = R^{(2)}$ and its value ranged from 1.7 to 2.0 to determine the optimum cut-off function parameters for graphene and CNTs.

Figure A1.2: (a) A reduced structure of graphene with inner and outer cut-off radii. (b) The variation of the bond strength with the radial distance. (c) The strain hardening of a graphene sheet under uniaxial tensile simulation.
Time step

Using a very small time step results in an extremely long calculation time [22]. For example, for a time step of 1 fs, million simulation steps are needed to model just one picosecond. On the other hand, a significantly large time step results in an unstable molecular system of overlapping atoms and consequently a rapid increase in the potential energy of the system due to the repulsive forces [22], as shown in Fig. A1.3. In order to achieve an acceptable accuracy in MD simulations, a time step in the range of 0.033 to 0.01 of the bond vibration period is recommended, which results in a time step ranging from a fraction of femtosecond to few femtoseconds [22,23]. The magnitude of the bond vibration period depends on the interatomic potential, material type/lattice structure, and temperature [22].

![Diagram](image.png)

Figure A1.3 The trajectories’ evolution of atoms with time: (a) the initial locations and velocities at time t, (b) the locations of the atoms when using appropriate time step ($\delta t \cong 0.033-0.01$ bond vibration period), and (c) the atoms overlapping when using too large time step (molecular structure explosion).

All MD simulations are being conducted under specified conditions. These ensembles are characterized by fixed values of the following thermodynamic variables: potential energy, temperature, pressure, volume, and total number of particles. The most used ensembles in MD simulations are: micro-canonical ensemble (NVE), isothermal-isobaric (NTP), and canonical ensemble (NVT). The key factor in obtaining reliable results is loading the system with a strain rate low enough to allow the system to respond properly to the applied load (i.e. conduct the heat that is formed due to the extremely high loading rate [24]).
Appendix 2: Eshelby Tensor in Micromechanical Model

The Eshelby tensor $[S_{RVE}^{\text{RVE}}]$ used in our Micromechanical models for simulating an infinite ($L/d=\infty$) cylindrical inclusion aligned along $x_1$-axis was given by [22,25] as follows (different terms have been defined in beginning of thesis):

\[
S_{1111} = 0 \tag{A2.1}
\]
\[
S_{2222} = S_{3333} = \frac{5 - 4\nu_o}{8(1-\nu_o)} \tag{A2.2}
\]
\[
S_{2233} = S_{3322} = \frac{4\nu_o - 1}{8(1-\nu_o)} \tag{A2.3}
\]
\[
S_{2211} = S_{3311} = \frac{\nu_o}{2(1-\nu_o)} \tag{A2.4}
\]
\[
S_{1122} = S_{1133} = 0 \tag{A2.5}
\]
\[
S_{1212} = S_{1313} = \frac{1}{4} \tag{A2.6}
\]

where $\nu_o$ is the Poisson ratio of the polymer matrix.
Appendix 3: Experimental Investigations

Experiments were performed to measure the morphology and dispersion quality of a typical CNT-epoxy composite. The obtained results from this analysis were used to define the curvature and agglomeration parameters in our investigation of the mechanical and interfacial properties of nanocomposite systems with realistic microstructures. MWCNTs (90% Purity) synthesized by the electric arc technique were obtained commercially. The average diameter and length of the CNTs are 13-18 nm and 1-12 μm. Figure A3.1 shows scanning electron micrograph (SEM) image of the as-received MWCNTs taken with a Quanta 250 field emission gun environmental scanning electron microscope.

Figure A3.1 SEM image of as-received MWCNTs.

Epoxy liquid based on a diglycidyl ether of bisphenol A (DGEBA) resin and triethylene tetramine (TETA) curing agent was purchased from Sigma-Aldrich Inc. The optimum properties of the cured epoxy system are obtained at a volume ratio of 1:2 parts hardening agent to the base resin. We prepared dogbone samples that were fractured using a tensile test on an electro-hydraulic servo-controlled testing machine. The fractured surfaces of the specimen were used in morphology and dispersion measurements for CNT-epoxy composites with weight percentages up to 4.0%. The samples were prepared using the following steps:
(v) Mixing the necessary weight fractions of CNT with ethanol and the suspension was stirred for 1 hour at 2000 rpm.

(vi) Heating the epoxy resin to 80°C to reduce its viscosity before being mixed with the CNT-ethanol suspension, the suspensions were stirred for 1 hour at 2000 rpm.

(vii) Evaporating the ethanol by placing the mixture in a vacuum oven at 100°C for 1 h.

(viii) Stirring the mixtures again for 1 h at 2000 rpm.

(ix) Sonicating the solution using a high intensity ultrasonic processor for 10 minutes at 500 W and 40 kHz.

(x) Adding the hardener in a 1:2 mixing ratio and stirring the mixture at 2000 rpm for 10 min.

(xi) Placing the mixture in a vacuum oven to remove any trapped air.

(xii) Pouring the mixture into dogbone molds.

(xiii) Leaving the samples to harden in a vacuum oven at 140°C for 8 h.

A uniform distribution of the CNTs in the prepared samples with CNT concentrations lower than 1% was verified by AFM and SEM imaging of their fractured surfaces, as shown in Fig. A3.2. The dispersed CNTs had a wide range of curvatures and could be assumed to be of a sinusoidal shape. At higher CNT concentrations, the dispersed nanotubes start to agglomerate in bundles with various sizes, as shown in Fig. A3.3.
Figure A3.2 CNTs distribution in the polymer matrix: (a) AFM and (b) SEM images of an epoxy polymer reinforced with uniformly distributed 1.0 wt.% of CNTs.

Figure A3.3 SEM images of an epoxy polymer reinforced with 4.0 wt.% of CNT.
References
7  N. Dewapriya, University of British Columbia, 2012.