Multiscale Modeling of CNT-Polymer Nanocomposites and Fuzzy Fiber Reinforced Polymer Composites for Strain and Damage Sensing

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Keywords: CNT, Nanocomposites, Fuzzy fiber, Piezoresistivity, Micromechanics, Multiscale Copyright 2014, Xiang Ren Multiscale Modeling of CNT-Polymer Nanocomposites and Fuzzy Fiber Reinforced Polymer Composites for Strain and Damage Sensing

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(ABSTRACT)

It has been observed that carbon nanotube (CNT)-polymer nanocomposite material has observable piezoresistive effect, that is to say that changes in applied strain may induce measurable changes in resistance. The first focus of the work is on modeling the piezoresistive response of the CNT-polymer nanocomposites by using computational micromechanics techniques based on finite element analysis. The in-plane, axial, the three dimensional piezoresistive responses of the CNT-polymer nanocomposites are studied by using 2D, axisymmetric, and 3D electromechanically coupled and multiscale finite element models. The microscale mechanisms that may have a substantial influence on the overall piezoresistivity of the nanocomposites, i.e. the electrical tunneling effect and the inherent piezoresistivity of the CNT, are included in microscale RVEs in order to understand their influence on macroscale piezoresistive response in terms of both the normalized change in effective resistivity and the corresponding effective gauge factor under applied strain. The computational results are used to better understand the driving mechanisms for the observed piezoresistive response of the material. The second focus of the work is on modeling the piezoresistive response of fuzzy fiber reinforced polymer composites by applying a 3D multiscale micromechanics model based on finite element analysis. Through explicitly accounting for the local piezoresistive response of the anisotropic interphase region, the piezoresistive responses of the overall fuzzy fiber reinforced polymer composites are obtained. The modeling results not only provide a possible explanation for the small gauge factors as observed in experiments, but also give guidance for the manufacture of fuzzy fiber reinforced polymer composites in order to achieve large, consistent, and predictable gauge factors. The third focus of the work is on modeling the coupled effect between continuum damage and piezoresistivity in the CNT-polymer nanocomposites by using computational micromechanics techniques based on a concurrent multiscale finite element analysis. The results show that there is a good correlation between continuum damage and piezoresistive response of the nanocomposites, which gives theoretical and modeling support for the use of CNT-polymer nanocomposites in structural health monitoring (SHM) applications for damage detections.

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Dedication

To my grandparents, parents, and wife.

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Contents

List of Figures				xii
\mathbf{Li}	List of Tables xxx			
1	Intr	oducti	on	1
2	Computational Micromechanics Modeling of Inherent Piezoresistivity in			
	CN'	T-Poly	mer Nanocomposites	7
	2.1	Introd	uction \ldots	7
	2.2	Multis	cale Model for the CNT-Polymer Nanocomposites	9
		2.2.1	Boundary Conditions and Effective Properties	19
		2.2.2	Piezoresistive Algorithm	23
	2.3	Result	s and Discussion	26
		2.3.1	Nanocomposite Piezoresistive Response Under Uniaxial Tension in the	
			CNT Alignment Direction	27
		2.3.2	Results for the Transverse Piezoresistive Response of the Nanocomposites	39
	2.4	Conclu	usions	51

3	Computational Micromechanics Modeling of Piezoresistivity in CNT-Polymer			
	Nanocomposites			
	3.1	Introd	uction \ldots	53
	3.2	Model	Description	54
		3.2.1	Mechanical Governing Differential Equations for the Microscale RVE	55
		3.2.2	Electrostatic Governing Differential Equations for the Microscale RVEs	57
		3.2.3	Boundary Conditions and Effective Properties	63
		3.2.4	Piezoresistive Algorithm	66
	3.3	Result	s and Discussion	68
		3.3.1	Plane-strain uniaxial tension test on the well-dispersed transverse hexag- onal RVE	69
		3.3.2	Plane-strain uniaxial tension test on the randomly dispersed transverse RVE	78
		3.3.3	Axial tension test on the axisymmetric RVE	82
	3.4	Conclu	usions	86
4	Modeling of Dispersion Effect on the Piezoresistivity of Carbon Nanotube-			
	ics Methods			
	4.1	Introd	uction	90
	4.2	Model	Description	93
		4.2.1	Schematics of the 3D computational multiscale model	93
		4.2.2	Computational procedures for the 3D multiscale model	96

	4.3	3 Results and Discussion			
		4.3.1 The first CNT dispersion scenario	98		
		4.3.2 The second and third CNT dispersion scenarios	103		
	4.4	Conclusions	110		
5	Mo	odeling of Electrostatic Properties of Fuzzy Fiber Reinforced Polyme			
	Con	Composites via Hierarchical Composite Cylinders Method			
	5.1	Introduction	112		
	5.2	Hierarchical CCM Modeling for Electrostatic Properties of Fuzzy Fiber Rein-			
		forced Polymer Composites	113		
		5.2.1 The governing equations for the electrostatic CCM model	116		
	5.3	Examples	119		
	5.4	Conclusions	125		
6	Con	nputational Multiscale Modeling and Characterization of Piezoresis	-		
	tivi	vity in Fuzzy Fiber Reinforced Polymer Composites			
6.1 Introduction \ldots		Introduction	127		
	6.2	Single Tow Piezoresistive Fragmentation Testing	129		
		6.2.1 Specimen Fabrication	129		
		6.2.2 Test Procedure	131		
	6.3	3D Computational Multiscale Model	133		
		6.3.1 Schematics of the 3D Computational Multiscale Model	133		
		6.3.2 Computational Procedures for the 3D Multiscale Model	135		

	6.4	Exper	imental Results and Discussion	140			
	6.5	Model	ing Results and Discussion	143			
		6.5.1	Modeling of FFRPC with Cylindrical Orthotropic or Randomly Ori- ented CNTs	143			
		6.5.2	Modeling of FFRPC with Sparse Regions of the CNT	151			
	6.6	Conclu	usions	153			
7	Con	lcurrer	nt Multiscale Modeling of Coupling between Continuum Damag	e			
	and	Piezo	resistivity in CNT-Polymer Nanocomposites	155			
	7.1	Introd	uction \ldots	155			
	7.2	Model	description	158			
		7.2.1	Modeling of Continuum Damage and Piezoresistive Effects in the CNT- Polymer Nanocomposites	158			
		7.2.2	The Multiscale Continuum Damage and Piezoresistivity Coupled Fi- nite Element Model	161			
	7.3	Result	s and Discussion	163			
		7.3.1	The Microscale Continuum Damage and Piezoresistivity Coupled Re- sponse of the Nanocomposites	164			
		7.3.2	The Multiscale Continuum Damage and Piezoresistivity Coupled Re- sponse of the Nanocomposites	169			
	7.4	Conclu	usions	174			
Bi	bliog	graphy		Bibliography 176			

Appendix A Periodic boundary conditions for the plane-strain uniaxial ten-

Appendix B Derivations of the effective gauge factors for the plane-strain tension tests 192

Appendix C Geometry correspondence between axial and transverse RVEs 194

Appendix D Verification on the finite element piezoresistive modeling work196

List of Figures

1.1 Fuzzy fiber material: a) A single fuzzy fiber with densely-packed and radially oriented CNTs on the surface (http://muri18.tamu.edu/). b) A single fuzzy fiber with densely-packed and randomly oriented CNTs on the surface. . . . 4

2.1	The hierarchical multiscale modeling of nanocomposites in which there are	
	well-dispersed and aligned CNTs	9

2.4 Schematic representation of the calculation of macroscale gauge factors for a) a general uniaxial tension tension test, b) a uniaxial tension test in the alignment direction of an effectively transversely isotropic nanocomposite, and c) a uniaxial tension test in the transverse direction of an effectively transversely isotropic nanocomposite.

26

- 2.5 The evolution of local strains and resistivities under applied macroscale strain increments for a CNT volume fraction of 0.20 and aspect ratio of 5 and for a CNT gauge factor corresponding to Case AU1. A potential difference of 1V is applied between the top and bottom edge of the microscale RVE. The results are shown in the form of contour plots of the axial strain component ε_{zz} and axial resistivity component ρ_{zz} in response to the applied homogeneous boundary strain which is linearly increased from 0% to 1%. The volume fraction of the CNT in the microscale RVE is 0.20, with an aspect ratio of 5, which are higher and lower, respectively, than typical CNT-polymer nanocomposite values, but are selected here to better view changes within the CNT.

- 2.7 Nanocomposite effective axial resistivities ρ_{zz}^{Eff} obtained from the axisymmetric microscale RVE in response to the applied boundary strain ε_0 for a CNT volume fraction of 0.005 and CNT aspect ratio of AR=300. a) Change of the effective resistivity component $\Delta \rho_{zz}^{\text{Eff}}$ as a function of the applied boundary strain of the microscale RVE for Case AU1 with $G^{\text{C}} = 2900$. b) $\Delta \rho_{zz}^{\text{Eff}}$ vs ε_0 for Case AU4 with $G^{\text{C}} = 1\text{E}13$. c) $\Delta \rho_{zz}^{\text{Eff}}$ vs ε_0 for Case AU5 with $G^{\text{C}} = 1\text{E}17$. d) $\Delta \rho_{zz}^{\text{Eff}}$ vs ε_0 in semi-log plot for the five CNT gauge factor cases listed in Table 2.4.

- 2.11 The distribution of local strains and resistivities of the plane-strain uniaxial tension in the 2-direction test at $\varepsilon_0 = 1\%$. a) Distribution of ε_{11} and ε_{22} for cases T1 and T6 at $\varepsilon_0 = 1\%$. b) Distribution of ρ_{11} and ρ_{22} for case T1 at $\varepsilon_0 = 1\%$. c) Distribution of ρ_{11} and ρ_{22} for case T6 at $\varepsilon_0 = 1\%$. The volume fraction of the CNTs in the microscale RVE is 0.60, which is higher than typical CNT-polymer nanocomposite volume fraction, but is selected here to better view changes within the CNTs.

2.15 The relative change of the effective resistivity components ρ_{22}^{Eff} of the nanocomposites in response to the applied boundary strain ε_0 of plane-strain uniaxial tension test for CNT volume fractions of 0.005, 0.01, 0.05, and 0.10. a) $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_{22}^{\text{Eff}}(0)} \times 100\%$ vs ε_0 for case T8 with $G^{\text{C}} = 1E14$. b) $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_{22}^{\text{Eff}}(0)} \times 100\%$ vs ε_0 for case T9 with $G^{\text{C}} = 1E17$.

46

48

55

- 2.16 Nanocomposite effective transverse resistivity component $\Delta \rho_{22}^{\text{Eff}}$ obtained from the transverse hexagonal microscale RVE in response to the applied boundary strain ε_0 of the plane-strain biaxial tension test, in which the volume fraction of the CNT is 0.005. a) Change of the effective resistivity component $\Delta \rho_{22}^{\text{Eff}}$ as a function of the applied boundary strain of the microscale RVE for cases T1 and T6 with $G^{\text{C}} = 2900$. b) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 for cases T4 and T9 with $G^{\text{C}} = 1\text{E17}$. c) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 in semi-log plot for the cases T1-T5. d) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 in semi-log plot for the cases T6-T10.

- 3.2 Microscale RVEs for the nanocomposites with 10% CNTs. a) is the transverse hexagonal microscale RVE for the well-dispersed and aligned CNTs. b) is the transverse microscale RVE for the aligned CNTs with random in-plane distribution, in which $W_2 = H_2$. c) is the axisymmetric microscale RVE, in which W'_1 goes to $\frac{\sqrt{3}W_1}{6}$ as the aspect ratio of the CNT $A = \frac{L_{CNT}}{2r_{CNT}}$ goes to infinity. ($\frac{\sqrt{3}W_1}{6}$ is the half distance between two adjacent CNTs in a)). Note that the aspect ratio used here is 20, which is only for demonstration purposes as the real aspect ratio used in the computations is much higher.
- a) The map of constant tunneling resistivities ρ_{tunnel} in the space of separation distance d and barrier height λ. b) The semi-log plot of the electrical tunneling resistivity ρ_{tunnel} with increase of separation distance d as λ is kept at 0.5 eV, 1.5 eV, and 2.5 eV respectively. The inset is the one in non semi-log plot. . . 60

3.4 a) The schematic illustration of the algorithm for obtaining the electrical tunneling resistivities in the polymer matrix. b)The contour distribution of isotropic resistivity in the hexagonal microscale RVE. c) The contour distribution of isotropic resistivity in the microscale RVE in which there are in-plane random aligned CNTs. d) The contour distribution of isotropic resistivity in the axisymmetric microscale RVE. Note that as the aspect ratio of the CNT is chosen to be 300, the RVE shown here is the zoomed in region focusing on the tip of the axisymmetric RVE. In b), c) and d), the volume percentages of the CNT are chosen to be the same of 10%vol, and the polymer matrixes are also chosen to be the same, i.e. the original resistivity is $10^{14}\Omega \cdot m$ and the height of barrier $\lambda = 0.75$ eV, and the corresponding cut-off distance $d_c = 4.78nm$.

- 3.5 Schematic representation of the calculation of macroscale gauge factors for
 a) a uniaxial tension test in the transverse directions of the nanocomposite
 specimen with aligned CNTs and b) an axial tension test in the alignment
 direction of an effectively transversely isotropic nanocomposite.
 64

- 3.8 The change of effective resistivities and gauge factors of the transverse hexagonal microscale RVEs at $\varepsilon_0 = 1\%$ with the change of volume fraction of the CNT. a) The effective resistivity component ρ_{22}^{eff} at $\varepsilon_0 = 1\%$ vs. the change of volume fraction of the CNT from 1% to 60%. b) The effective gauge factor G_2^{eff} at $\varepsilon_0 = 1\%$ vs. the change of volume fraction of the CNT from 1% to 60%. 75

- 3.9 The contour distribution of isotropic resistivity in the chosen two random transverse RVEs, in both of which the volume fraction of the CNT is 10%. Note that the scale bars are different for the contours. a) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the first random microscale RVE with $\lambda = 1.4$ eV and for the transverse hexagonal RVE with $\lambda = 1.4$ eV. b) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the second random microscale RVE with $\lambda = 1.4$ eV. b) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the second random microscale RVE with $\lambda = 1.4$ eV. The dashed box regions denote areas in which there are stronger electrical tunneling paths due to the nonuniformity of the distribution of the CNTs.
- 3.10 The contour distribution of isotropic resistivity in the chosen two random transverse RVEs, in both of which the volume fraction of the CNT is 10%. Note that the scale bars are different for the contours. a) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the first random microscale RVE with $\lambda = 0.5$ eV and for the transverse hexagonal RVE with $\lambda = 0.5$ eV. b) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively at the applied boundary strain of 0.0% and 1.0% respectively of resistivity at the applied boundary strain of 0.0% and 1.0% respectively at the applied boundary strain of 0.0% and 1.0% respectively of the second random microscale RVE with $\lambda = 0.5$ eV.
- 3.11 Comparison of the relative change of effective resistance of the hexagonal microscale RVE and the random microscale RVEs with the change of boundary strain ε_0 under plane-strain uniaxial tension test. a) Comparison of $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the hexagonal microscale RVE and the random microscale RVEs as $\varepsilon_0 = 0.0\% 1.0\%$, in all of which there are 10%vol CNTs and $\lambda = 1.4$ eV. b) Comparison of $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the hexagonal microscale RVEs as $\varepsilon_0 = 0.0\% 1.0\%$, in all of which there are 10%vol CNTs and $\lambda = 1.4$ eV. b) Comparison of $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the hexagonal microscale RVE and the random microscale RVEs as $\varepsilon_0 = 0.0\% 1.0\%$, in all of which there are 10%vol CNTs and $\lambda = 0.5$ eV.

- 3.12 Distribution of the resistivity component ρ_{zz} in the axisymmetric RVEs under axial tension test, in which the aspect ratio of the CNT is 300, $\lambda = 1.4$ eV, and $G_c = 2900$ (G_c is converted to $g_{zz} = 2.84 \times 10^2 \Omega \cdot m$ as inputs for our model (Ren and Seidel, 2013a)). Note that the scale bars are different for the two sets of contours. a) Distribution of ρ_{zz} in the 1%vol RVE with the boundary strain applied at $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 0.1\%$. b) Distribution of ρ_{zz} in the 20%vol RVE with the boundary strain applied at $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 0.1\%$. 84

- 4.1 Gauge factors of the CNT polymer nanocomposites under tension and compression as found in the literature (Kang et al., 2006b; Zhang et al., 2006; Wichmann et al., 2009; Kang et al., 2009; Bautista-Quijano et al., 2010; Oliva-Aviles et al., 2011; Ferreira et al., 2012b; Ku-Herrera et al., 2013). 91

Schematics of the 3D computational multiscale micromechanics model for the 4.2nanocomposite specimen under uniaxial tension or compression test. a) The macroscale nanocomposite specimen under uniaxial tension or compression test. b) The mesoscale RVE (1 mm^3) for the nanocomposite material within the specimen. Note that in real computations the number of elements used is 8000, i.e. 64000 subelements. c) One single hexahedron element within the mesoscale RVE. d) Illustration of the CNT bundle within the subelement. e) The nanoscale RVE representing the CNT bundle. Note that ~ on the coordinate system denotes the macroscale whereas the [^]denotes the nanoscale, with the mesoscale denoted with an unmodified X_i coordinate system. . . . 93 4.3The diagram of CNT dispersions for the 3D multiscale model. Note that the subcells correspond to the subelements of the mesoscale RVE. Also note that the scenarios of a) to g) illustrated here are in 1-3 plane. 95The 3D multiscale model for scenario 1. a) Illustration of the mesoscale RVE 4.4with well-dispersed, randomly oriented, and 1.0% wt nanoscale RVEs. b) Illustration of the 1.0% wt nanoscale RVE under the transformed mesoscale strain field of $\varepsilon' = R\varepsilon R^{-1}$, in which R can be found in Ref. (Ren et al., 2014) (Displacement magnification factor: 37). 99 Strain distribution of the mesoscale RVE under the macroscale strain field 4.5of $(\tilde{\varepsilon}_{33} = 1\%, \tilde{\varepsilon}_{11} = -\nu_{31}^{\text{eff}}\tilde{\varepsilon}_{33}, \tilde{\varepsilon}_{22} = -\nu_{32}^{\text{eff}}\tilde{\varepsilon}_{33})$. Within the mesoscale RVE there are hexagonally packed and randomly oriented 1.0% wt CNTs in each 101 The relative change of effective resistivity $\Delta \rho_{33}^{\rm eff} / \rho_{33(0)}^{\rm eff}$ of the mesoscale RVE 4.6when the macroscale strain $\tilde{\varepsilon}_{33}$ is from 0% to $\pm 1\%$. Note that for every subelement the nanoscale RVE is randomly oriented with the CNT gauge 102

- 4.7 The 3D multiscale model for scenarios 2 and 3. a) Illustration of the 62.5%vol nanoscale RVE under the transformed mesoscale strain of ε' = RεR⁻¹, in which R can be found in Ref. [36] (Displacement magnification factor: 68).
 b) Illustration of the 1%wt mesoscale RVE with well-dispersed, randomly oriented, and 62.5%vol nanoscale RVEs for scenario 2. c) Illustration of the 1%wt mesoscale RVE with partially dispersed and partially columned, randomly oriented, and 62.5%vol nanoscale RVEs for scenario 3. 105
- 4.8 The relative change of effective resistivity $\Delta \rho_{33}^{\text{eff}} / \rho_{33(0)}^{\text{eff}}$ of the mesoscale RVE when the macroscale strain $\tilde{\varepsilon}_{33}$ is from 0% to $\pm 1\%$ for scenarios 2 and 3. . . 108
- 5.1 Schematic of (a) a cross-ply laminate with mixture of non-fuzzy and fuzzy glass fibers, (b) individual fuzzy fiber corresponding to the composite cylinder model (representative of an aligned all fuzzy fiber laminate plies), with the first (innermost) layer being the structural glass fiber, the second layer being the nanocomposite interphase where there are densely packed and radially oriented CNTs, and the third layer being the pure polymer matrix, (c) $\Delta\theta$, Δr , and Δz segment of the nanocomposite interphase region, (d) well-dispersed, densely packed CNTs within the interphase corresponding to a hexagonal packing originating at the glass fiber-nanocomposite interface (the hat denotes local MWCNT scale), (e) nanocomposite composite cylinders model. 115

- 5.3 The change of effective conductivities of the composites with the change of volume fraction of glass fiber/glass fiber core by using the Mori-Tanaka method.122

a) Optical image of a single fuzzy fiber tow spread apart by tweezers (Scale 6.1bar: 2 cm). b) Field emission SEM (FESEM) image of single fuzzy fibers within the fuzzy fiber tow (Scale bar: 100 μ m). c) SEM image of single fuzzy fibers within the fuzzy fiber tow, on which the CNTs are peeled off (Scale bar: $20 \ \mu m$). Note that the diameter of the structural fiber core is measured as 6 μ m. d) FSEM image of a section of a single fuzzy fiber (Scale bar: 2 μ m). e) FESEM image of the CNTs on the fuzzy fibers (Scale bar: $1 \ \mu m$). 1306.2Illustration of placing the fuzzy fiber tow into the dogbone mold. 130a) Optical image of the dogbone specimen, within which the fuzzy fiber tow 6.3is embedded. b) Close up of the connection between the fuzzy fiber tow and the copper wire through the conductive silver epoxy. c) SEM image of the single fuzzy fibers infused by the polymer matrix within the fuzzy fiber tow region of the dogbone specimen (Scale bar: 50 μ m). d) Close up of the fuzzy fibers infused by polymer matrix (Scale bar: $20 \ \mu m$). 132a) In-house fabricated tensile machine with the dogbone specimen being tested. 6.4 b) Close up of the dogbone specimen gripped on the tensile machine. . . . 132Schematics of the computational multiscale model for the dogbone specimen 6.5under the single tow fragmentation test. a) The macroscale FEM for the dogbone specimen under the single tow fragmentation test. b) The microscale hexagonal RVE (FEM) for the fuzzy fiber tow infused by polymer matrix. c) A single fuzzy fiber infused by polymer matrix. d) The CNT-polymer nanocomposite interphase of the fuzzy fiber. e) The nanoscale hexagonal RVE for the CNT-polymer nanocomposite interphase of fuzzy fiber (The axis of the

CNT is in \hat{Y}_1 direction). Note that $\tilde{}$ on the coordinate system denotes the

- 6.7 The computational multiscale model for the mechanical problem. a) Distribution of von Mises strain $\tilde{\varepsilon}_{v}$ within the dogbone specimen under tensile tension test. b) Distribution of von Mises strain ε_{v} within the 3%vol microscale RVE under the macroscale strain field of $\tilde{\varepsilon}^{avg}$. c) Distribution of von Mises strain $\hat{\varepsilon}_{v}$ within the 60%vol nanoscale RVE under the microscale strain field of $\varepsilon' = R\varepsilon R^{-1}$. Note that in this showing case the CNTs are assumed to be cylindrically orthotropic within the fuzzy fiber interphase region. 138

- 6.10 The piezoresistive response of the fuzzy fiber dogbone specimen with applied external loadings. a) Correlation between measured resistance and linear loading, b) Correlation between measured resistance and cyclic loading, c) Correlation between measured resistance and paused loading, d) Correlation between measured resistance and paused loading, d) Correlation between measured relative change of resistance and applied boundary displacement. 143

- 6.13 The piezoresistive response of FFRPC with CO interphases, in which the volume fraction of the CNT within the nanoscale RVE is varied from 60% 90%, and the thickness of the interphase is varied from 1 μm to 3 μm. a) ρ₃₃^{eff} vs. ε₃₃^{avg} at 60%vol of the CNT, b) ρ₃₃^{eff} vs. ε₃₃^{avg} at 60%vol of the CNT, b) ρ₃₃^{eff} vs. ε₃₃^{avg} at 70%vol of the CNT, c) ρ₃₃^{eff} vs. ε₃₃^{avg} at 80%vol of the CNT, and d) ρ₃₃^{eff} vs. ε₃₃^{avg} at 90%vol of the CNT (Unit: Ω·m). Note that in a), b) and c) as the inherent piezoresistivity of the CNT has negligible effect, the curves are the ones corresponding to the electrical tunneling effect only.
- 6.14 The piezoresistive response of FFRPC with interphases of randomly aligned CNTs. Note that the volume fraction of the CNT within the nanoscale RVE is varied from 60% - 90%, and the thickness of the interphase is kept at 2 μ m. 150

- 7.2 The computational algorithm for implementing the multiscale finite element analysis. Note that the variables in '~' are macroscale variables, otherwise they are microscale variables. The macroscale element index $n_1 \in [1, n_M]$, in which n_M is the total number of macroscale elements, the microscale element index $n_2 \in [1, n_m]$, in which n_m is the total number of microscale elements, and the time step $\tau \in [0, \tau_T]$, in which τ_T is the total number of time steps. 162

The contours of the stiffness tensor component \tilde{C}_{22} , the von Mises strain $\tilde{\varepsilon}_{v}$,	
and the conductivity $\tilde{\kappa}_{22}$ of the macroscale specimen at applied boundary	
strain $\tilde{\varepsilon}_{22}^{\rm B}$ of 0.25% and 0.50% respectively. a1) Contour of \tilde{C}_{22} at $\tilde{\varepsilon}_{22}^{\rm B}$ =	
0.25%, b1) Contour of $\tilde{\varepsilon}_{v}$ at $\tilde{\varepsilon}_{22}^{B} = 0.25\%$, c1) Contour of $\tilde{\kappa}_{22}$ at $\tilde{\varepsilon}_{22}^{B} = 0.25\%$,	
a2) Contour of \tilde{C}_{22} at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$, b2) Contour of $\tilde{\varepsilon}_{v}$ at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$, c2)	
Contour of $\tilde{\kappa}_{22}$ at $\tilde{\varepsilon}_{22}^{\rm B} = 0.50\%$. Note that the conductivity $\tilde{\kappa}_{22}$ is the inverse	
of resistivity $\tilde{\rho}_{22}$.	174
The coupled damage-piezoresistive response of the macroscale specimen as the	
applied macroscale boundary strain $\tilde{\varepsilon}_{22}^{\rm B}$ is from 0% to 0.50% (Stress unit: Pa;	
Resistivity unit: $\Omega \cdot m$).	175
Comparison of my modeling work and the ones as obtained from ABAQUS	
for the linear elastic problem. a) Contour of ε_{11} from my modeling work, b)	
Contour of ε_{11} from ABAQUS, c) Contour of σ_{11} from my modeling work, d)	
Contour of σ_{11} from ABAQUS. Note that the mesh contains 12803 nodes and	
25012 elements	197
Comparison of my modeling work and the ones as obtained from ABAQUS for	
the electrostatic problem without electron hopping. a) Contour of E_1 from my	
modeling work, b) Contour of EPG_1 from ABAQUS, c) Contour of E_2 from	
my modeling work, d) Contour of EPG ₂ from ABAQUS. Note that $E_i = -\frac{\partial \Phi}{\partial x_i}$	
and $EPG_i = \frac{\partial \Phi}{\partial x_i}$	198
The contour of resistivity component ρ_{22} of the hexagonal nanoscale RVE with	
	The contours of the stiffness tensor component C_{22} , the von Mises strain $\tilde{\varepsilon}_{v}$, and the conductivity $\tilde{\kappa}_{22}$ of the macroscale specimen at applied boundary strain $\tilde{\varepsilon}_{22}^{B}$ of 0.25% and 0.50% respectively. a1) Contour of \tilde{C}_{22} at $\tilde{\varepsilon}_{22}^{B} =$ 0.25%, b1) Contour of $\tilde{\varepsilon}_{v}$ at $\tilde{\varepsilon}_{22}^{B} = 0.25\%$, c1) Contour of $\tilde{\kappa}_{22}$ at $\tilde{\varepsilon}_{22}^{B} = 0.25\%$, a2) Contour of \tilde{C}_{22} at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$, b2) Contour of $\tilde{\varepsilon}_{v}$ at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$, c2) Contour of $\tilde{\kappa}_{22}$ at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$. Note that the conductivity $\tilde{\kappa}_{22}$ is the inverse of resistivity $\tilde{\rho}_{22}$

10%
vol CNTs under plane-strain biaxial tension test of $\varepsilon_0 = 1.0\%~(\lambda = 0.5~{\rm eV}).199$

List of Tables

2.1	Boundary conditions for the 2D microscale RVEs as shown in Fig. 3.2a and	
	Fig. 3.2b	20
2.2	Electrostatic boundary conditions for obtaining the effective electrical con-	
	ductivities.	22
2.3	Mechanical, electrical and geometric parameters for the CNT and EPON 828	
	polymer matrix (Hammerand et al., 2007; Seidel and Lagoudas, 2009; Ebbesen	
	et al., 1996; Schadler et al., 1998; Arris, 2000). The conductivity of the CNT	
	listed here is the initial conductivity with zero strain. \ldots \ldots \ldots \ldots	27
2.4	The conversions from CNT gauge factor to CNT axial piezoresistive strain	
	coefficient g_{zz}^{C} , in which case AU1 is converted at the strain $\varepsilon_{C} = 1.5\%$ as in	
	Ref. (Stampfer et al., 2006), and cases AU2-AU5 are converted at the strain	
	$\varepsilon_{\rm C} = 1\%$. For each case it assumed that all other $g_{ij}^{\rm C}$ are zero	28
2.5	The effective nanocomposite gauge factors \mathbf{G}^{Eff} at strain levels of 0.1%, 0.4%	
	0.7% and $1.0%$ for CNT-polymer nanocomposites having CNT volume frac-	
	tions of 0.005 and 0.01 and CNTs with CNT gauge factors corresponding to	
	cases AU1 through AU5 for a CNT aspect ratio of 300	38

2.6	The conversions from CNT gauge factor to CNT piezoresistive strain coeffi-	
	cients, in which cases T1 and T6 are converted at the strain $\varepsilon_{\rm C}$ = 1.5% as	
	in Ref. (Stampfer et al., 2006), and the remaining cases are converted at the	
	strain $\varepsilon_{\rm C} = 1\%$. For each case, it is assumed that all other $g_{ij}^{\rm C}$ are zero	40
2.7	The effective nanocomposite gauge factors \mathbf{G}^{Eff} at strain levels of 0.1%, 0.4%,	
	0.7%, and $1.0%$ of the plane-strain uniaxial and biaxial tension tests for CNT-	
	polymer nanocomposites having CNT volume fractions of 0.005 and CNTs	
	with CNT gauge factors corresponding to cases T1 through T10	50
3.1	Boundary conditions for the 2D microscale RVEs as shown in Fig. 3.2a,	
	Fig. 3.2b, and Fig. 3.2c.	65
3.2	Electrostatic boundary conditions for obtaining the effective electrical con-	
	ductivities of the 2D microscale RVEs as shown in Fig. 3.2a, Fig. 3.2b, and	
	Fig. 3.2c. Note that κ_{ij}^{eff} are effective conductivities, which can be inversed to	
	obtain the effective resistivities ρ_{ij}^{eff}	66
3.3	The volume averaged resistivity component $\rho_{\text{CNT}(22)}^{\text{avg}}$ of the CNT and the ef-	
	fective resistivity component $\rho_{\rm RVE(22)}^{\rm eff}$ of the 10% vol transverse hexagonal mi-	
	croscale RVE at the applied boundary strains of ε_0 = 0.0% and ε_0 = 1.0%	
	respectively of the plane-strain uniaxial tension test	73
3.4	The volume averaged resistivity component $\rho^{\rm avg}_{\rm CNT(22)}$ of the CNT and the ef-	
	fective resistivity component $\rho_{\rm RVE(22)}^{\rm eff}$ of the 60% vol transverse hexagonal mi-	
	croscale RVE at the applied boundary strains of ε_0 = 0.0% and ε_0 = 1.0%	
	respectively of the plane-strain uniaxial tension test	74
3.5	The effective resistivity component $\rho_{22}^{\rm eff}$ and the effective gauge factor ${\rm G}_2^{\rm eff}$ at	
	the percolating volume fraction and at 20% vol	76

- 4.1The effective mechanical properties of the mesoscale RVE for scenario 1 (Unit: GPa). Note that 'vertical' represents that the CNTs align in X_3 direction, 'transverse' represents that the CNTs are randomly dispersed in $X_1 - X_2$ plane, and 'random' represents that the CNTs are randomly dispersed in the 100 The zero-strain resistivities $\rho_{33(0)}^{\text{eff}}$ (Unit: $\Omega \cdot \mathbf{m}$), tensile gauge factors $\mathbf{G}_{33}^{\text{eff}(\mathbf{T})}$, 4.2and compressive gauge factors $G_{33}^{\text{eff}(C)}$ of the mesoscale RVE for scenario 1. Note that the gauge factors are computed at $\tilde{\varepsilon}_{33} = 1\%$ 1034.3 The effective mechanical properties of the mesoscale RVE for scenarios 2 and 3 (Unit: GPa). Note that the nanoscale RVE is randomly oriented for all of the 849 subelements. 106The zero-strain resistivities $\rho_{33(0)}^{\text{eff}}$ (Unit: $\Omega \cdot \mathbf{m}$), tensile gauge factors $\mathbf{G}_{33}^{\text{eff}(\mathbf{T})}$, 4.4and compressive gauge factors $G_{33}^{eff(C)}$ of the mesoscale RVE for scenario 2. Note that the gauge factors are computed at $\tilde{\varepsilon}_{33} = 1\%$ 107The zero-strain resistivities $\rho_{33(0)}^{\text{eff}}$ (Unit: $\Omega \cdot \mathbf{m}$), tensile gauge factors $\mathbf{G}_{33}^{\text{eff}(\mathbf{T})}$, 4.5and compressive gauge factors $G_{33}^{eff(C)}$ of the mesoscale RVE for scenario 3. Note that the gauge factors are computed at $\tilde{\varepsilon}_{33} = 1\%$ 109

Chapter 1

Introduction

Carbon nanotubes (CNT) are cylindrical fullerenes with closed or open ends. Since their discovery by Iijima (1991), they have drawn great attention of the scientific and engineering communities. While single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT) have radii on the order of nanometers, they can have their lengths ranging from less than one micrometer to several millimeters. The CNT' unique molecular structures make them yield extraordinary material properties. For example, it has been found that the SWCNT have Young's modulus on the average of 1000 GPa (Yu et al., 2000a), which is five time higher than the one of steel, and in the mean while is only of one fifth to one sixth of the density. The tensile strengths of MWCNT are observed to be from 11 GPa (Yu et al., 2000b) to 150 GPa (Demczyk et al., 2002), which are one to two orders higher than the one of steel. In addition, it is found that a SWCNT has a room-temperature thermal conductivity of 3500 W·m⁻¹·K⁻¹ along its axis (Pop et al., 2006), which is one order higher than copper. Due to the CNT's multifaceted extraordinary material properties, it is beneficial to add the CNT as a strengthening phase in the composite materials to improve their overall performances.

The CNT-polymer nanocomposite material is a type of polymer composites added by CNTs as a strengthening phase. To date, several kinds of CNT-polymer nanocomposites have been shown to have linear piezoresistive responses with small loadings of SWCNT or MWCNT (Zhang et al., 2006; Kang et al., 2006b, 2009; Bautista-Quijano et al., 2010; Oliva-Aviles et al., 2011; Ferreira et al., 2012a,b). For example, Zhang et al. (2006) found in the small strain range of 1% that MWCNT/Polycarbonate (PC) films loaded with 5% wt MWCNT can yield a strain sensitivity approximately 3.5 times that of a commercial (metallic) strain gauge. Kang et al. (2006b) found the gauge factor of sensors made of SWNT/PMMA composites to range from about 1 to 5 when the weight percentage of SWCNT range from 0.5% wt to 10% wt, with the higher sensitivity being achieved using 3% wt to 10% wt SWCNT. Kang et al. (2009) reported that for the SWNT/Polyimide composites sensors, the maximum gauge factor is achieved at a concentration just above the percolation threshold concentration (0.05%wt SWCNT) with a magnitude of 4.21. Bautista-Quijano et al. (2010) reported the gauge factors of thin films made of Polysulfone (PSF) and dispersed MWCNT to range from 0.48 to 0.73 when the weight percentage of MWCNT is between 0.2% to 1.0% wt. Ferreira et al. (2012b) reported that the maximum gauge factor ranges up to 6.2 for the hot pressed SWCNT/PVDF composites when the weight percentage of SWCNT is just below 2% wt. For aligned MWCNT/PSF films with 0.5% wt MWCNTs aligned by application of AC electric fields during processing, Oliva-Aviles et al. (2011) reported a gauge factor of 2.78 ± 0.42 for tensile loading in the MWCNT alignment direction. It has also been observed that at a concentration just above the CNT electrical percolation threshold, the piezoresistive stress coefficient of SWCNT/Polyimide nanocomposites exceeds those of metallic materials (aluminum) by two orders of magnitude (Kang et al., 2009). Such piezoresistive properties make CNT-polymer nanocomposites very attractive in the manufacturing of high gauge-factor light-weight strain gauges.

In addition, researchers have also found that the piezoresistive response of the CNT-polymer nanocomposites can be an indicator of damage events within the material (Park et al., 2007; Li and Chou, 2008; Saafi, 2009; Kim et al., 2010; Alexopoulos et al., 2010; Vadlamani et al., 2012b,a; Cardoso et al., 2012; Heeder et al., 2012). For example, by using double-matrix composite techniques, the carbon fiber fracture events were inherently sensed by the piezore-sistive response of CNT-polymer nanocomposites, and it was found that the piezoresistivity
of the nanocomposites can well capture the fiber fracture events (Park et al., 2007). Saafi (2009) used wireless cement-CNT sensors for damage detection in concrete structures, and it was found that the carbon nanotube networks can in-situ detect crack initiation and propagation. Vadlamani et al. (2012b) dispersed 0.3%wt-0.5%wt CNTs into epoxy, and through measuring the piezoresistivity of the CNT-polymer nanocomposites they studied the in-situ sensing of nonlinear deformation, damage initiation, and growth within the material. Therefore, in contrast to the customary surface strain measurements obtained from commercial strain gauges bonded to the surface of structures, the CNT-polymer nanocomposite strain gauges have the potential to be directly embedded in structural composites during composite processing to provide internal and in-situ strain and damage sensing.

While there are ample experimental evidences demonstrating the piezoresistive response of CNT-polymer nanocomposites, the mechanisms governing piezoresistivity of CNT-polymer nanocomposites are less clear in terms of relative magnitude and interactions. At present, several mechanisms are believed to contribute to the piezoresistive response of CNT-polymer nanocomposites. For example, Fernberg et al. (2009) indicated that the geometric change of the specimen will have an effect on its macroscale resistance behavior. Kang et al. (2009) have indicated that the piezoresistive response of macroscale nanocomposite material originates from the tunneling effect (Simmons, 1963; Fuhrer et al., 2000; Budlum and Lu, 2001; Li et al., 2007; Xia and Curtin, 2007; Li and Chou, 2008; Li et al., 2008; Theodosiou and Saravanos, 2010; Hu et al., 2012) between conducting inclusions (CNTs) at the nanoscale under compression or tension. It has been observed both experimentally and in modeling that mechanical deformation of CNTs can directly lead to significant changes in their conductance (Peng and Cho, 2000), indicating CNTs are themselves good strain sensors due to inherent piezoresistivity. In order to aide in the design of piezoresistive nanocomposite strain gauges with tailored sensitivities, it is necessary to develop an understanding of the underlying mechanisms at the micro and nanoscales which govern the macroscale piezoresistive response.

The fuzzy fiber material (Bower et al., 2000; Thostenson et al., 2002; Zhu et al., 2003; Zhao

et al., 2005; Ci et al., 2005; Mathur et al., 2008; Garcia et al., 2008; Sager et al., 2009; Yamamoto et al., 2009, 2012; Wood et al., 2012; Sebastian et al., 2014) is an engineering material that has a carbon, glass, ceramic, or alumina structural fiber core, with dense CNT "forest" coated on the fiber surface, as observed in Fig. 1.1. In the fuzzy fiber reinforced polymer



Figure 1.1: Fuzzy fiber material: a) A single fuzzy fiber with densely-packed and radially oriented CNTs on the surface (http://muri18.tamu.edu/). b) A single fuzzy fiber with densely-packed and randomly oriented CNTs on the surface.

composites (FFRPC), the CNTs on the structural fiber surface form a multifunctional interphase region, which can provide enhanced load transfer, damage resistance, higher thermal and electrical conductivities, and electromechanical coupling in the form of piezoresistivity. For example, it is found that fuzzy fibers coated with randomly oriented MWCNTs and aligned MWCNTs can have 71% and 11% increase respectively in interfacial shear strength over the unsized and untreated fibers (Sager et al., 2009). It is measured that FFRPC with alumina-fiber cores have a high electrical conductivity of >100 S/m and an enhancement of thermal conductivity (~1 W/m K) (Yamamoto et al., 2012). Sebastian et al. (2014) integrated fuzzy fiber sensors into composite structures to explore their internal sensing abilities. It is found that the fuzzy fiber sensors with a gauge factor of 1.6 - 2.3, which is similar to conventional strain gauges, can provide sensing over large sections and in locations not accessible

to conventional strain gauging techniques. The multi-functionality of the interphase region makes FFRPC good candidates for multifunctional applications such as structural health monitoring (SHM), electromagnetic shielding, fire resisting and deicing (Yamamoto et al., 2012; Sebastian et al., 2014). In contrast to the customary surface strain measurements, FFRPC strain gauges have the potential to be directly embedded in structural composites during composite processing to provide internal strain sensing (Veedu et al., 2006; Boger et al., 2008; Yamamoto et al., 2012). In order to aid in the design of FFRPC strain gauges with tailored sensitivities for SHM applications, it is necessary to develop an understanding of the underlying mechanisms which govern the macroscale piezoresistive response.

To date, researchers have spent significant amount of efforts in modeling different kinds of material properties, such as mechanical, thermal, electrical, acoustic, and magnetic properties among others. Modeling efforts are of importance not only for better understanding of the underling physics, but also sometimes for analysis, prediction, and optimization purposes. For the CNT-polymer nanocomposite materials, different modeling techniques and methods such as molecular dynamics approaches (Frankland et al., 2003; Griebel and Hamaekers, 2004; Adnan et al., 2007; Zhu et al., 2007) and continuum micromechanics approaches (Fisher and Brinson, 2001; Fisher et al., 2002, 2003; Bradshaw et al., 2003; Buryachenko and Roy, 2005; Liu et al., 2005; Liu and Brinson, 2006; Seidel and Lagoudas, 2006, 2009; Seidel and Puydupin-Jamin, 2011; Ren and Seidel, 2013a,b; Spanos and Kontsos, 2008; Hadjiev et al., 2006; Wagner, 2002) have been applied either independently or in a combination manner (Li and Chou, 2003; Odegard et al., 2003, 2004; Seidel and Lagoudas, 2008). Such models are substantially multiscale, and are developed not only based on observations and approximations of engineering physics, but also based on rigorous mathematics such as calculus and statistics.

In this study, multiscale micromechanics piezoresistive models based on finite element analysis have been developed to systematically study the piezoresistive mechanisms of CNTpolymer nanocomposites and FFRPC. The contents of the dissertation are arranged as follows: Chapter 2 discusses the work on modeling the influence of inherent piezoresistivity of

the CNT on the overall piezoresistive response of the nanocomposites; Chapter 3 discusses the work on modeling the coupled effect of electrical tunneling and inherent piezoresistive effects within the CNT-polymer nanocomposites; Chapter 4 discusses the work on modeling the dispersion effect on the piezoresistive response of the CNT-polymer nanocomposites via using a 3D multiscale computational model; Chapter 5 discusses the work on modeling the initial electrostatic properties of fuzzy fiber reinforced polymer composites; Chapter 6 discusses the work on computational multiscale modeling and characterization of the piezore-

sistivity within the fuzzy fiber reinforced polymer composites; last but not least Chapter 7 gives modeling work of the coupled effect of damage and piezoresistivity within the CNT-polymer nanocomposites.

Computational Micromechanics Modeling of Inherent Piezoresistivity in CNT-Polymer Nanocomposites

2.1 Introduction

As introduction in Chapter 1, CNT-polymer nanocomposites have been shown to have linear piezoresistive responses with small loadings of single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT) (Zhang et al., 2006; Kang et al., 2006b, 2009; Bautista-Quijano et al., 2010; Oliva-Aviles et al., 2011; Ferreira et al., 2012a,b). A mechanism is associated with the CNTs themselves which have been shown to have a considerable inherent effect which should not be neglected. It has been observed both experimentally and in modeling that mechanical deformation of CNTs can directly lead to significant changes in their conductance (Peng and Cho, 2000), indicating CNTs are themselves good strain sensors due to inherent piezoresistivity. Efforts to quantify the inherent piezoresistivity of CNTs have taken the form of both characterization and modeling experiments. For example, Chen

et al. employed molecular dynamics simulations and quantum transport theory to study the electrical properties of (12,0) zigzag carbon nanotubes under different uniaxial strains, and found that a 1% strain can result in a 6.4% decrease in resistance (Chen and Weng, 2007). Tight-binding and zone-folding approximations have been used to predict the strain sensitivity of a carbon nanotube, which is found to be based on its chiral indices (n,m), and varies widely with the electrical structures (Cullinan and Culpepper, 2010; Anantram et al., 1999). Experimentally, Tombler et al. (2000) applied strain to a suspended CNT using AFM tips and observed that the conductance of the CNT could change by as much as two orders of magnitude under the applied strains. Stampfer et al. (2006) measured the relative differential resistance sensitivity for a metallic SWNT of up to 27.5% per nanometer of deflection from which a piezoresistive gauge factor of a SWNT of up to 2900 was extracted. To our knowledge, there has been no clear discussion and quantification as to what magnitude of inherent CNT piezoresistivity is needed to achieve macroscale nanocomposite gauge factors on the order of 2 to 5 if this mechanism was indeed the driving force behind the nanocomposite piezoresistive response.

In this study, a computational multiscale micromechanics model based on finite elements analysis is developed and used to determine the changes in macroscale resistance (i.e. effective macroscale piezoresistance) due to changes at the microscale associated with CNT deformation and inherent piezoresistivity. The effects of CNT geometry, local volume fraction, and inherent piezoresistive coefficients on the macroscale piezoresistivity are studied parametrically. The results are discussed in the context of experimentally observed gauge factors for nanocomposites and the strength of electromechanical coupling needed to achieve observed responses.

2.2 Multiscale Model for the CNT-Polymer Nanocomposites

In the CNT-polymer nanocomposites, the strains in the CNTs may have an effect on their resistivities, therefore the mechanical and electrical properties of the nanocomposites are one way coupled. In other words, the mechanical properties of the domain may influence its electrical properties, but not vice versa. Typically, the dispersion and shape of CNTs in the CNT-polymer nanocomposites may be complicated, e.g. the CNTs can be curved along their axes, randomly oriented, and bundled with the other CNTs. In order to focus the present study on the potential impact of inherent piezoresistivity of CNTs on the macroscale piezoresistive response of nanocomposites, we have selected a multiscale idealization as shown in Fig. 3.1. In this representation, the CNTs are assumed to be well-dispersed, aligned and perfectly bonded to the surrounding polymer. The governing differential equations describing mechanical and electrostatic responses of the nanocomposites are given below:



Figure 2.1: The hierarchical multiscale modeling of nanocomposites in which there are welldispersed and aligned CNTs

Chapter 2

Mechanical Governing Differential Equations at the Macroscale

For quasi-static conditions and omitting body forces, conservation of linear momentum at the macroscale can be written in cartesian coordinate system as

$$\tilde{\sigma}_{ij,j} = 0 \tag{2.1}$$

where the overscript " \sim " denotes variables at the macroscale. Note that the summation convention is used with i, j ranging from 1 to 3 and the comma denotes spatial differentiation. The infinitesimal strain displacement relations at the macroscale are given by

$$\tilde{\varepsilon}_{ij} = \frac{1}{2} (\tilde{u}_{i,j} + \tilde{u}_{j,i}) \tag{2.2}$$

The macroscale constitutive relation for the mechanical boundary can be expressed as:

$$\tilde{\sigma}_{ij} = C_{ijkl}^{\text{Eff}} \tilde{\varepsilon}_{kl} \tag{2.3}$$

where C_{ijkl}^{Eff} are the effective macroscale stiffness components which are obtained from the volume averaged stress-strain response at the microscale as

$$\langle \sigma_{ij} \rangle = C_{ijkl}^{\text{Eff}} \langle \varepsilon_{kl} \rangle \tag{2.4}$$

where the brackets $\langle \cdot \rangle$ denote volume averaging over the appropriate microscale representative volume element (RVE). The mechanical boundary value problem is completed through the specification of the boundary conditions which can be given by

$$\tilde{u}_i = \tilde{u}_i^0 \quad \text{on } S_u \tag{2.5a}$$

and

$$\tilde{t}_i = \tilde{n}_j \tilde{\sigma}_{ij} = \tilde{t}_i^0 \quad \text{on } S_\sigma$$

$$(2.5b)$$

where the complete macroscale boundary is specified as the union of S_u and S_{σ} . It is noted that the macroscale effective mechanical properties obtained from the microscale boundary value problem are independent of the macroscale boundary conditions, and thus, need only be determined once at the initiation of the piezoresistive simulations. The macroscale

Chapter 2

effective elastic properties can therefore be obtained by using either computational micromechanics method (Hammerand et al., 2007) or by using composite cylinder method (Seidel and Lagoudas, 2006).

Electrostatic Governing Differential Equations at the Macroscale

The steady-state conservation of charge equation at the macroscale can be denoted in cartesian coordinate system as:

$$\tilde{J}_{i,i} = 0 \tag{2.6}$$

where \tilde{J}_i is the current density at the macroscale. The macroscale electrical field is obtained as the negative of the gradient of the macroscale potential as

$$\tilde{E}_i = -\tilde{\Phi}_{,i} \tag{2.7}$$

where \tilde{E}_i and $\tilde{\Phi}$ are the electric field and electric potential respectively at the macroscale. In an analogous manner as in the macroscale mechanical boundary value problem, the constitutive relation for the macroscale electrical boundary value can be expressed as

$$\tilde{E}_i = \rho_{ij}^{\text{Eff}} \tilde{J}_j \tag{2.8a}$$

or

$$\tilde{J}_i = \kappa_{ij}^{\text{Eff}} \tilde{E}_j \tag{2.8b}$$

where ρ_{ij}^{Eff} and κ_{ij}^{Eff} are the effective macroscale resistivity and conductivity components respectively, which are obtained from the volume averaged current density-electric field response at the microscale as

$$\langle E_i \rangle = \rho_{ij}^{\text{Eff}} \langle J_j \rangle \tag{2.9a}$$

or

$$\langle J_i \rangle = \kappa_{ij}^{\text{Eff}} \langle E_j \rangle \tag{2.9b}$$

where the brackets again denote volume averaging over the appropriate microscale RVE. The electrical boundary value problem is completed through the specification of the boundary conditions which can be given by

$$\tilde{\Phi} = \tilde{\Phi}^0 \quad \text{on } S_{\Phi} \tag{2.10a}$$

and

$$\tilde{n}_i \tilde{J}_i = \tilde{n}_i \tilde{J}_i^0 \quad \text{on } S_J \tag{2.10b}$$

where the complete macroscale boundary is specified as the union of S_{Φ} and S_J . It is noted that the macroscale effective electrical properties obtained from the microscale boundary value problem are independent of the macroscale electrical boundary conditions. However, due to the piezoresistivity at the microscale, the macroscale effective electrical properties do depend on the macroscale mechanical boundary conditions. As such, the effective electrical properties must be determined at each mechanical load step. The macroscale effective electrical properties must therefore be obtained in an incremental manner using either computational micromechanics method or composite cylinder method for specific material symmetries of electrical material properties (Seidel and Lagoudas, 2009; Ren and Seidel, 2011).

Mechanical Governing Differential Equations for the Microscale RVE

The 3D microscale RVE for aligned CNT nanocomposites (Fig. 3.1) can be reduced to two 2D RVEs in order to save computational time. As seen in Fig. 3.2a, due to high aspect ratios (≥ 200) of CNTs, the transverse properties of the nanocomposites are typically modeled using the regular hexagonal array RVE under in-plane strain assumption. The annulus areas represent the cross-sections of CNTs, and the remaining area is pure polymer matrix. Correspondingly, a plane strain periodic finite element model is constructed to model the piezoresistive response of the nanocomposites in the transverse directions. On the other hand, for cases where the loading is axisymmetric, for example in the uniaxial tension test, the axial properties of the nanocomposites are modeled by using a 2D axisymmetric RVE



Figure 2.2: Microscale RVEs for the nanocomposites with well-dispersed and aligned CNTs. a) is the transverse hexagonal microscale RVE with the volume fraction of the CNTs being 10%. b) is the axisymmetric microscale RVE with the volume fraction of the CNT being 0.5% vol and the aspect ratio of the CNT being 20 (The aspect ratio used here is only for demonstration purposes as the real aspect ratio used in the computations is much higher (≥ 200)). X_1 and X_2 are in the same plane as X_r and X_{θ} . W_1 is the width of the hexagonal microscale RVE in X_1 direction, and W_2 is the width of the hexagonal microscale RVE in X_2 direction. L is the length of the axisymmetric microscale RVE in X_z (or X_3) direction, L_{CNT} is the length of CNT, and R is the half distance between two adjacent CNTs.

that is axisymmetric about the axis (Fig. 3.2b). The highlighted area is CNT, and the remaining area is pure polymer matrix. Correspondingly, an axisymmetric finite element model is constructed to model the axial piezoresistive response of the nanocomposites.

For quasi-static conditions omitting body forces, conservation of linear momentum for the microscale RVE can be written in cartesian coordinate system as

$$\sigma_{ij,j} = 0 \tag{2.11}$$

where under the plane strain assumptions of the transverse hexagonal RVE σ_{13} and σ_{23} are zero. For the axisymmetric microscale RVE, it is more convenient to express conservation of linear momentum in cylindrical coordinates as

Chapter 2

$$\frac{\partial \sigma_{rr}}{\partial r} + \frac{\partial \sigma_{rz}}{\partial z} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} = 0$$
(2.12a)

$$\frac{\partial \sigma_{rz}}{\partial r} + \frac{\partial \sigma_{zz}}{\partial z} + \frac{\sigma_{rz}}{r} = 0$$
(2.12b)

where it is noted that terms involving θ shear components or differentiation with respect to θ have been eliminated from the general cylindrical form. The infinitesimal strain-displacement relations for the microscale RVE are given in Cartesian coordinates by

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \tag{2.13}$$

where under the plane strain assumptions for the transverse hexagonal RVE $\varepsilon_{13} = 0$, $\varepsilon_{23} = 0$, and $\varepsilon_{33} = 0$. For the axisymmetric microscale RVE the strain-displacement relations in cylindrical coordinates are given as

$$\varepsilon_{rr} = \frac{\partial u_r}{\partial r}, \quad \varepsilon_{\theta\theta} = \frac{u_r}{r}, \quad \varepsilon_{zz} = \frac{\partial u_z}{\partial z},$$

$$\varepsilon_{\theta z} = 0, \quad \varepsilon_{rz} = \frac{1}{2} \left(\frac{\partial u_z}{\partial r} + \frac{\partial u_r}{\partial z} \right), \quad \varepsilon_{r\theta} = 0.$$
(2.14)

At the microscale, the CNT annulus and polymer matrix can be assumed to be isotropic linear elastic materials (Saito et al., 1998) such that their constitutive relationships can be denoted with the Lame constants as

$$\sigma_{ij} = 2\mu^{\rm C}\varepsilon_{ij} + \lambda^{\rm C}\varepsilon_{kk}\delta_{ij} \tag{2.15a}$$

$$\sigma_{ij} = 2\mu^{M}\varepsilon_{ij} + \lambda^{M}\varepsilon_{kk}\delta_{ij}$$
(2.15b)

where the superscripts C and M on the material properties denote CNT and polymer matrix respectively, and the standard relationships $\mu = \frac{E}{2(1+\nu)}$ and $\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}$ hold. The boundary conditions on the microscale RVE can be expressed as either traction or displacement boundary conditions by

$$t_i = n_j \tilde{\sigma}_{ij}(X_k) \tag{2.16a}$$

$$u_i = x_j \tilde{\varepsilon}_{ij}(\tilde{X}_k) \tag{2.16b}$$

such that in general the macroscale and microscale RVE stresses and strains can be related to one another through microscale volume averages as

$$\tilde{\sigma}_{ij}(\tilde{X}_k) = \langle \sigma_{ij} \rangle$$
 (2.17a)

$$\tilde{\varepsilon}_{ij}(\tilde{X}_k) = \langle \varepsilon_{ij} \rangle$$
 (2.17b)

where $\tilde{\sigma}_{ij}(\tilde{X}_k)$ and $\tilde{\varepsilon}_{ij}(\tilde{X}_k)$ are the macroscale stress and strain at a macroscale material point \tilde{X}_k which the microscale RVE represents. Note that in Eqs. (3.1) - (3.3), i, j, k = 1, 2, 3 in the Cartesian coordinate system of the transverse hexagonal microscale RVE, while i, j, k = r, θ, z in the cylindrical coordinate system of the axisymmetric microscale RVE.

Electrostatic Governing Differential Equations for the Microscale RVEs

The steady-state conservation of charge equation for the microscale RVE can be denoted in Cartesian coordinates as:

$$J_{i,i} = 0 \tag{2.18}$$

where J_i is the current density, and where under in-plane electrostatic assumptions $J_{3,3} = 0$. For the axisymmetric microscale RVE, it is again more convenient to express conservation of charge in cylindrical coordinates as

$$\frac{\partial J_r}{\partial r} + \frac{\partial J_z}{\partial z} + \frac{1}{r}J_r = 0$$
(2.19)

where it is noted that terms involving θ current density components or differentiation with respect to θ have been eliminated from the general cylindrical form. The microscale RVE electric field is obtained as the negative of the gradient of the microscale potential as

$$E_i = -\Phi_{,i} \tag{2.20}$$

where E_i (i = 1, 2, 3) and Φ are the electric field and electric potential respectively as applied in Cartesian coordinate system at the microscale and where under in-plane electro-static

assumptions it is noted that $E_3 = 0$. For the axisymmetric microscale RVE the electric field is obtained from the potential in cylindrical coordinates as

$$E_r = -\frac{\partial \Phi}{\partial r} \tag{2.21a}$$

$$E_z = -\frac{\partial \Phi}{\partial z} \tag{2.21b}$$

where it is noted that terms involving the differentiation with respect to θ have been eliminated from the general cylindrical form. For the microscale RVEs, Ohm's law can be written as

$$E_i = \rho_{ij}^{\rm C} J_j \tag{2.22a}$$

$$E_i = \rho_{ij}^{\mathrm{M}} J_j \tag{2.22b}$$

where the superscripts C and M on the resistivities denote CNT and polymer matrix, respectively, such that the inverses of Eq. (3.6a) and (3.6b) yield the electrical conductivities of the CNT and polymer matrix, respectively, as

$$J_i = \kappa_{ij}^{\rm C} E_j \tag{2.23a}$$

$$J_i = \kappa_{ij}^{\mathrm{M}} E_j \tag{2.23b}$$

Note that in Eq. (3.6) and Eq. (2.23), i, j, k = 1, 2, 3 in the Cartesian coordinate system of the transverse hexagonal microscale RVE, while i, j, k = r, θ, z in the cylindrical coordinate system of the axisymmetric microscale RVE.

As the pure polymer matrix is not expected to be piezoresistive, the resistivity remains fixed under the applied strains. However, the CNTs are expected to exhibit inherent piezoresistivity such that the instantaneous resistivity, $\rho_{ij}^{\rm C}$ is a function of the local strain state within the CNT and can therefore be written as

$$\rho_{ij}^{\mathcal{C}} = \rho_{ij}^{\mathcal{C}0} + \Delta \rho_{ij}^{\mathcal{C}} \tag{2.24}$$

in which ρ_{ij}^{C0} are the initial zero strain resistivities of the CNT, and $\Delta \rho_{ij}^{C}$ are the change in resistivities induced by inherent piezoresistive effect of the CNT as obtained from

$$\Delta \rho_{ij}^C = \mathbf{g}_{ijkl}^C \varepsilon_{kl} \tag{2.25}$$

16

The g_{ijkl}^{C} are the piezoresistive strain coefficient components of the fourth order piezoresistive coefficient tensor of the CNT which in general has 81 components. However, due to the symmetry of both the resistivity and strain, i.e.

$$\Delta \rho_{ij}^C = \Delta \rho_{ji}^C \tag{2.26a}$$

$$\varepsilon_{kl} = \varepsilon_{lk} \tag{2.26b}$$

one may write

$$\mathbf{g}_{ijkl}^{\mathbf{C}} = \mathbf{g}_{jikl}^{\mathbf{C}} \tag{2.27a}$$

$$\mathbf{g}_{ijkl}^{\mathbf{C}} = \mathbf{g}_{ijlk}^{\mathbf{C}} \tag{2.27b}$$

The piezoresistive constitutive equation can therefore be denoted in Voigt notation as

$$\left\{ \begin{array}{c} \Delta\rho_{1}^{\mathrm{C}} \\ \Delta\rho_{2}^{\mathrm{C}} \\ \Delta\rho_{3}^{\mathrm{C}} \\ \Delta\rho_{3}^{\mathrm{C}} \\ \Delta\rho_{4}^{\mathrm{C}} \\ \Delta\rho_{5}^{\mathrm{C}} \\ \Delta\rho_{6}^{\mathrm{C}} \end{array} \right\} = \left[\begin{array}{c} g_{11}^{\mathrm{C}} & g_{12}^{\mathrm{C}} & g_{13}^{\mathrm{C}} & g_{14}^{\mathrm{C}} & g_{15}^{\mathrm{C}} & g_{16}^{\mathrm{C}} \\ g_{21}^{\mathrm{C}} & g_{22}^{\mathrm{C}} & g_{23}^{\mathrm{C}} & g_{25}^{\mathrm{C}} & g_{26}^{\mathrm{C}} \\ g_{31}^{\mathrm{C}} & g_{32}^{\mathrm{C}} & g_{33}^{\mathrm{C}} & g_{34}^{\mathrm{C}} & g_{35}^{\mathrm{C}} & g_{36}^{\mathrm{C}} \\ g_{41}^{\mathrm{C}} & g_{42}^{\mathrm{C}} & g_{43}^{\mathrm{C}} & g_{44}^{\mathrm{C}} & g_{45}^{\mathrm{C}} & g_{46}^{\mathrm{C}} \\ g_{51}^{\mathrm{C}} & g_{52}^{\mathrm{C}} & g_{53}^{\mathrm{C}} & g_{54}^{\mathrm{C}} & g_{55}^{\mathrm{C}} & g_{56}^{\mathrm{C}} \\ g_{61}^{\mathrm{C}} & g_{62}^{\mathrm{C}} & g_{63}^{\mathrm{C}} & g_{64}^{\mathrm{C}} & g_{65}^{\mathrm{C}} & g_{66}^{\mathrm{C}} \\ g_{61}^{\mathrm{C}} & g_{62}^{\mathrm{C}} & g_{63}^{\mathrm{C}} & g_{64}^{\mathrm{C}} & g_{65}^{\mathrm{C}} & g_{66}^{\mathrm{C}} \\ \end{array} \right] \left\{ \begin{array}{c} \varepsilon_{1} \\ \varepsilon_{2} \\ \varepsilon_{3} \\ \varepsilon_{3} \\ \varepsilon_{4} \\ \varepsilon_{5} \\ \varepsilon_{5} \\ \varepsilon_{5} \\ \varepsilon_{5} \end{array} \right\}$$
(2.28)

in which the number of the piezoresistive strain coefficients g_{ij}^{C} is reduced to 36 with the Voigt notation correspondence in Cartesian coordinates given by

$$\Delta \rho_1^{\rm C} = \Delta \rho_{11}^{\rm C}, \quad \Delta \rho_2^{\rm C} = \Delta \rho_{22}^{\rm C}, \quad \Delta \rho_3^{\rm C} = \Delta \rho_{33}^{\rm C}$$
$$\Delta \rho_4^{\rm C} = \Delta \rho_{23}^{\rm C}, \quad \Delta \rho_5^{\rm C} = \Delta \rho_{13}^{\rm C}, \quad \Delta \rho_6^{\rm C} = \Delta \rho_{12}^{\rm C}$$
$$\varepsilon_1 = \varepsilon_{11}, \quad \varepsilon_2 = \varepsilon_{22}, \quad \varepsilon_3 = \varepsilon_{33}$$
$$\varepsilon_4 = \varepsilon_{23}, \quad \varepsilon_5 = \varepsilon_{13}, \quad \varepsilon_6 = \varepsilon_{12}$$
(2.29)

Similarly, in Eq. (2.28) the Voigt notation correspondence to cylindrical components is given by:

$$\Delta \rho_1^{\rm C} = \Delta \rho_{rr}^{\rm C}, \quad \Delta \rho_2^{\rm C} = \Delta \rho_{\theta\theta}^{\rm C}, \quad \Delta \rho_3^{\rm C} = \Delta \rho_{zz}^{\rm C}$$

Chapter 2

$$\Delta \rho_4^{\rm C} = \Delta \rho_{\theta z}^{\rm C}, \quad \Delta \rho_5^{\rm C} = \Delta \rho_{rz}^{\rm C}, \quad \Delta \rho_6^{\rm C} = \Delta \rho_{r\theta}^{\rm C}$$
$$\varepsilon_1 = \varepsilon_{rr}, \quad \varepsilon_2 = \varepsilon_{\theta\theta}, \quad \varepsilon_3 = \varepsilon_{zz}$$
$$\varepsilon_4 = \varepsilon_{\theta z}, \quad \varepsilon_5 = \varepsilon_{rz}, \quad \varepsilon_6 = \varepsilon_{r\theta}$$
(2.30)

Based on CNT geometry and composition¹, the CNT piezoresistive strain coefficients are at most of transversely isotropic symmetry, and can therefore be expressed as

$$\begin{cases} \Delta \rho_{1}^{C} \\ \Delta \rho_{2}^{C} \\ \Delta \rho_{3}^{C} \\ \Delta \rho_{3}^{C} \\ \Delta \rho_{4}^{C} \\ \Delta \rho_{5}^{C} \\ \Delta \rho_{5}^{C} \\ \Delta \rho_{6}^{C} \\ \Delta \rho_{6}^{C} \\ \Delta \rho_{6}^{C} \\ \Delta \rho_{6}^{C} \\ \end{pmatrix} = \begin{bmatrix} g_{11}^{C} & g_{12}^{C} & g_{13}^{C} & 0 & 0 & 0 \\ g_{12}^{C} & g_{13}^{C} & g_{13}^{C} & 0 & 0 & 0 \\ g_{13}^{C} & g_{13}^{C} & g_{33}^{C} & 0 & 0 & 0 \\ 0 & 0 & 0 & g_{44}^{C} & 0 & 0 \\ 0 & 0 & 0 & 0 & g_{44}^{C} & 0 \\ 0 & 0 & 0 & 0 & 0 & g_{66}^{C} \\ \end{bmatrix} \begin{cases} \varepsilon_{1} \\ \varepsilon_{2} \\ \varepsilon_{3} \\ 2\varepsilon_{4} \\ 2\varepsilon_{5} \\ 2\varepsilon_{6} \\ \end{cases}$$
(2.31)

The number of independent components of the g_{ij}^C matrix is thus reduced to 5 with $g_{66}^C = \frac{g_{11}^C - g_{12}^C}{2}$. However, $g_{ij}^C = g_{ji}^C$ is based on an assumption which still needs to be further verified by either laboratory or lower length scale computational experiments as current efforts in this area have only explored the axial component, g_{33}^C . It is further noted that Eq. (2.31) can be reduced according to the assumptions regarding zero strain components for both the plane strain hexagonal and axisymmetric microscale RVEs as indicated above. The electrical boundary conditions on the microscale RVE can be expressed as either current density or potential conditions by

$$n_i J_i = n_i \tilde{J}_i(\tilde{X}_k) \tag{2.32a}$$

$$\Phi = x_i \tilde{\mathbf{E}}_i (\tilde{X}_k) \tag{2.32b}$$

such that in general the macroscale and microscale RVE current densities and electric fields can be related to one another through microscale volume averages as

$$\tilde{J}_i(\tilde{X}_k) = \langle J_i \rangle$$
 (2.33a)

¹Observing that the piezoresitive stress coefficient matrix for Germanium and Silicon displays diagonal symmetry (Smith, 1954), we assume this to likewise be the case for the piezoresistive strain coefficient matrix for the CNT.

$$\tilde{E}_i(\tilde{X}_k) = \langle E_i \rangle$$
 (2.33b)

where $\tilde{J}_i(\tilde{X}_k)$ and $\tilde{E}_i(\tilde{X}_k)$ are the macroscale current density and electric field at a macroscale material point \tilde{X}_k which the microscale RVE represents. Finally, as the local CNT resistivity according to Eq. (2.31) is now a function of the local strain in the CNT which in turn is influenced by the specific mechanical boundary conditions being imposed from the macroscale, the CNT and hence effective nanocomposite conductivities will therefore be functions of the applied mechanical loads at the macroscale.

Chapter 2

2.2.1 Boundary Conditions and Effective Properties

Mechanical Boundary Conditions

The macroscale material's effective elastic material properties can be obtained by constructing strain energy equivalence between the microscale RVE and the effective homogeneous representation using homogeneous periodic mechanical boundary conditions (Bensoussan et al., 1978). In the present work, periodic displacement boundary conditions consistent with certain desired uniform macroscale strain states are applied to the microscale RVEs which are known to be good representations for aligned well-dispersed fiber arrangements. The uniform strain fields chosen here are consistent with those present in macroscale planestrain tension tests and uniaxial tension test, which could be used to get effective elastic properties for the nanocomposites from the volume averaged stress and strain relationships provided in Eq. (2.4) (Hammerand et al., 2007). Herein the focus is on the piezoresistive effect, thus the choice of the tests are to demonstrate the magnitude of the impact of different strain states on the effective piezoresistive response of the nanocomposite material. The detailed periodic mechanical boundary conditions are listed in Table 3.1. It can be noted that under the in-plane strain assumption, the displacement field components u_1 and u_2 for the transverse hexagonal microscale RVE are independent of X_3 , while under the axisymmetric assumption, the displacement field components u_r and u_z for the axisymmetric microscale

$Chapter \ 2$

Table 2.1: Boundary conditions for the 2D microscale RVEs as shown in Fig. 3.2a andFig. 3.2b.

Type of test	B.C.s
Uniaxial tension test for the	$t_r(\mathbf{R}, X_\mathbf{z}) = t_z(\mathbf{R}, X_\mathbf{z}) = 0$
axisymmetric microscale RVE of	
Fig. 3.2b	$u_r(X_r, \frac{\mathrm{L}}{2}) - u_r(X_r, -\frac{\mathrm{L}}{2}) = 0$
	$u_z(X_{\mathbf{r}}, \frac{\mathbf{L}}{2}) - u_z(X_{\mathbf{r}}, -\frac{\mathbf{L}}{2}) = \varepsilon_0 \mathbf{L}$
Plane-strain uniaxial tension test for	$u_1(\frac{W_1}{2}, X_2) - u_1(-\frac{W_1}{2}, X_2) = -\nu'_{21}\varepsilon_0 W_1^{a}$
transverse hexagonal microscale RVE	
of Fig. 3.2a	$u_2(\frac{W_1}{2}, X_2) - u_2(-\frac{W_1}{2}, X_2) = 0$
	$u_1(X_1, \frac{W_2}{2}) - u_1(X_1, -\frac{W_2}{2}) = 0$
	$u_2(X_1, \frac{W_2}{2}) - u_2(X_1, -\frac{W_2}{2}) = \varepsilon_0 W_2$
Plane-strain biaxial tension test for	$u_1(\frac{W_1}{2}, X_2) - u_1(-\frac{W_1}{2}, X_2) = \varepsilon_0 W_1$
transverse hexagonal microscale RVE	
of Fig. 3.2a	$u_2(\frac{W_1}{2}, X_2) - u_2(-\frac{W_1}{2}, X_2) = 0$
	$u_1(X_1, \frac{W_2}{2}) - u_1(X_1, -\frac{W_2}{2}) = 0$
	$u_2(X_1, \frac{W_2}{2}) - u_2(X_1, -\frac{W_2}{2}) = \varepsilon_0 W_2$

^a $\nu'_{21} = \frac{\nu_{21}^{\text{Eff}} + \nu_{31}^{\text{Eff}} \nu_{23}^{\text{Eff}}}{1 - \nu_{32}^{\text{Eff}} \nu_{23}^{\text{Eff}}}$. See Appendix A for detailed derivations.

RVE are independent of X_{θ} . The strain ε_0 corresponds to the strain on a macroscale material point under tension, and is quasi-statically increased within the linear elastic range.

In general, the effective elastic properties can be obtained from the strain energy equivalency between the microstructural representation (i.e. the RVE) and an effective homogeneous material having the same exterior geometry and boundary conditions. The equivalency can be expressed as

$$\langle \sigma_{ij}\varepsilon_{ij}\rangle = \langle W^{\rm RVE}\rangle = \langle W^{\rm Eff}\rangle = \langle \sigma_{ij}^{\rm Eff}\varepsilon_{ij}^{\rm Eff}\rangle$$
 (2.34)

where σ_{ij}^{Eff} and $\varepsilon_{ij}^{\text{Eff}}$ denote the stress and strain fields in the homogenous material representation. Through the application of the Hill-Mandel theorem, the energy equivalency can be expressed as

$$\langle \sigma_{ij} \rangle \langle \varepsilon_{ij} \rangle = \langle \sigma_{ij}^{\text{Eff}} \rangle \langle \varepsilon_{ij}^{\text{Eff}} \rangle = \langle C_{ijkl}^{\text{Eff}} \varepsilon_{kl}^{\text{Eff}} \rangle \langle \varepsilon_{ij}^{\text{Eff}} \rangle = C_{ijkl}^{\text{Eff}} \langle \varepsilon_{kl}^{\text{Eff}} \rangle \langle \varepsilon_{ij}^{\text{Eff}} \rangle$$
(2.35)

As both the microstructural RVE and effective homogeneous representation are subjected to the same displacement boundary conditions $\langle \varepsilon_{ij} \rangle = \langle \varepsilon_{ij}^{\text{Eff}} \rangle$, and thus Eq. (2.4) is recovered. It can be shown that C_{ijkl}^{Eff} obtained in this manner under the assumptions of linear elastic perfectly bonded phases within the microstructure is independent of the strains associated with the applied displacements, i.e. of ε_0 .

Electrostatic Boundary Conditions

In an analogous manner as in the mechanical problem, the macroscale material's effective electrostatic material properties can be obtained by constructing electrical energy equivalence between the microscale RVE and the effective one with homogeneous periodic electrical boundary conditions applied. In the present work, periodic potential boundary conditions consistent with certain desired uniform electric field states are applied to the microscale RVEs, as listed in Table 3.2. Under the in-plane electrostatic assumption, the potential field Φ for the transverse hexagonal microscale RVE is independent of X_3 , while under the axisymmetric assumption, the potential field Φ for the axisymmetric microscale RVE is

v	0
Type of test	B.C.s
For obtaining κ_{zz}^{Eff} (κ_{33}^{Eff}) in the	$\Phi(X_{\mathrm{r}}, \frac{\mathrm{L}}{2}) - \Phi(X_{\mathrm{r}}, -\frac{\mathrm{L}}{2}) = \mathrm{E}_{0}\mathrm{L}$

axisymmetric microscale RVE $J_r(\mathbf{R}, X_z) = 0$

For obtaining $\kappa_{11}^{\rm Eff}$ in the

For obtaining κ_{22}^{Eff} in the

For obtaining κ_{12}^{Eff} in the

transverse hexagonal RVE

transverse hexagonal RVE

Table 2.2: Electrostatic boundary conditions for obtaining the effective electrical conductivif

transverse hexagonal RVE $\Phi(\frac{W_1}{2}, X_2) - \Phi(-\frac{W_1}{2}, X_2) = E_0 W_1$

independent of X_{θ} .

In general, the electrical conductivities can be obtained from the electrical energy equivalency between the microstructural representation (i.e. the RVE) and an effective homogeneous material having the same exterior geometry and boundary conditions. The equivalency can be expressed as

$$\langle J_i E_i \rangle = \langle W^{\text{RVE}} \rangle = \langle W^{\text{Eff}} \rangle = \langle J_i^{\text{Eff}} E_i^{\text{Eff}} \rangle$$
 (2.36)

 $\Phi(X_1, \frac{W_2}{2}) - \Phi(X_1, -\frac{W_2}{2}) = 0$

 $\Phi(X_1, \frac{W_2}{2}) - \Phi(X_1, -\frac{W_2}{2}) = E_0 W_2$

 $\Phi(\frac{W_1}{2}, X_2) - \Phi(-\frac{W_1}{2}, X_2) = E_0 W_1$

 $\Phi(X_1, \frac{W_2}{2}) - \Phi(X_1, -\frac{W_2}{2}) = E_0 W_2$

 $\Phi(\frac{W_1}{2}, X_2) - \Phi(-\frac{W_1}{2}, X_2) = 0$

where J_i^{Eff} and E_i^{Eff} denote the current density and electric field in the homogenous material representation. Through the application of the electrical analogy to the Hill-Mandel theorem, the energy equivalency can be expressed as

$$\langle J_i \rangle \langle E_i \rangle = \langle J_i^{\text{Eff}} \rangle \langle E_i^{\text{Eff}} \rangle = \langle \kappa_{ij}^{\text{Eff}} E_j^{\text{Eff}} \rangle \langle E_i^{\text{Eff}} \rangle = \kappa_{ij}^{\text{Eff}} \langle E_j^{\text{Eff}} \rangle \langle E_i^{\text{Eff}} \rangle$$
(2.37)

As both the microstructural RVE and effective homogeneous representation are subjected to the same potential boundary conditions, $\langle E_i \rangle = \langle E_{ij}^{\text{Eff}} \rangle$, and thus Eq. (2.9b) is recovered. While it can be shown that κ_{ij}^{Eff} obtained in this manner under the assumptions of linear material behavior and perfectly connected phases within the microstructure is independent of the electric fields associated with the applied potentials, i.e. of E_0 , it must be noted

however, that due to the inherent piezoresistivity of the CNTs, the effective conductivity is a function of the strains associated with the applied displacements, i.e. $\kappa_{ij}^{\text{Eff}} = \kappa_{ij}^{\text{Eff}}(\varepsilon_{kl})$.

2.2.2 Piezoresistive Algorithm

An incremental algorithm for determining the piezoresistive response of the nanocomposites is developed within a finite element framework, and is applied to the 2D microscale RVEs as shown in Fig. 3.2. The Galerkin and Ritz methods are used, respectively, for the formulation of in-plane and axisymmetric piezoresistive finite element models. The mechanical and electrostatic finite element formulations are coupled together sequentially with the mechanical formulation used to first obtain the strains in the microscale RVEs which are then used as inputs for the electrostatic formulation. The detailed piezoresistive algorithm is provided in Fig. 2.3. In step 1 of the algorithm, the electrostatic potential boundary value problems as



Figure 2.3: The piezoresistive algorithm of the finite element model

identified in Table 3.2 are applied to the initial undeformed microscale RVEs resulting in potential distributions, and the electrical energy equivalence is used to obtain the conductivities of the effective microscale RVEs. In step 2, the first mechanical load increments are

applied to the microscale RVEs according to the boundary conditions identified in Table 3.1, resulting in the local strain distributions. In step 3, the local strains in the CNT obtained from step 2 are used in the piezoresistive constitutive relation to determine changes in the local resistivities of the CNTs. In step 4, the same electrostatic potential boundary value problems from step 1 are applied again to the microscale RVEs with updated local electrical properties of the CNT, with the electrical energy equivalency enforced to obtain the effective conductivities $\kappa_{ij}^{\text{Eff}}(\varepsilon_{kl})$ of the effective microscale RVEs. Step 2 through step 4 are then repeated for subsequent loading increments. From this process the effective electrical properties of the microscale RVEs with inherent piezoresistive effect of the CNT can be obtained as a function of the applied macroscale homogeneous strain, i.e. the load dependent but reversible macroscale effective piezoresistive response.

In order to compare with measures more commonly used in experiments, the effective resistivities $\rho_{ij}^{\text{Eff}}(\varepsilon_{kl})$ (inverse of $\kappa_{ij}^{\text{Eff}}(\varepsilon_{kl})$) obtained in the plane-strain tension tests and uniaxial tension test can be converted into macroscale nanocomposite gauge factors. As shown schematically in Fig. 6.2, the gauge factor for a uniaxial tension test can be expressed in general as

$$G = \frac{\frac{\Delta R}{R}}{\varepsilon} = \frac{\frac{\rho^{f} \frac{L^{\prime}}{Af} - \rho^{0} \frac{L^{0}}{A0}}{\rho^{0} \frac{L^{0}}{A0}}}{\varepsilon_{0}}$$
(2.38)

where G is the gauge factor, ε is the applied strain, and R is the resistance measured between two electrodes. The change in resistance can be expressed in terms of the initial resistivity, ρ^0 , the undeformed distance between electrodes, L^0 , the undeformed electrode area, A^0 , and their corresponding measures in the deformed configuration of ρ^f , L^f , and A^f , respectively. For the uniaxial tension test, the deformed distance between electrodes and deformed electrode area can be expressed in terms of the applied strain as $L^f = L^0(1 + \varepsilon_0)$ and $A^f = A^0(1 - \nu_{31}\varepsilon_0)(1 - \nu_{32}\varepsilon_0)$, respectively, so that G in Eq. (2.38) becomes

$$G = \frac{1}{\varepsilon_0} \left(\frac{\rho^f}{\rho^0} \frac{1 + \varepsilon_0}{(1 - \nu_{31}\varepsilon_0)(1 - \nu_{32}\varepsilon_0)} - 1 \right)$$
(2.39)

For the metal alloy wires commonly used in strain gauges, the initial and final resistivities are the same, so that the gauge factor is governed by the isotropic Poisson's ratio, and results

in an approximately linear relationship between normalized change in resistance and strain (i.e. with G as the slope of the curve) for small strains.

However, the inherent piezoresistivity of the CNTs means that the initial and final resistivities of the nanocomposite will differ from one another, introducing additional non-linearity in the gauge factor. As such, the effective gauge factor for the nanocomposite as obtained from a uniaxial tension test in the CNT alignment direction (i.e. from the axisymmetric RVE) would be determined as

$$\mathbf{G}^{\text{Eff}} = \frac{1}{\varepsilon_0} \left(\frac{\rho_{33}^{\text{Eff}}(\varepsilon_0)}{\rho_{33}^{\text{Eff}}(0)} \frac{1 + \varepsilon_0}{(1 - \nu_{31}^{\text{Eff}} \varepsilon_0)^2} - 1 \right)$$
(2.40)

where the transverse direction is the isotropic plane such that $\nu_{31}^{\text{Eff}} = \nu_{32}^{\text{Eff}} = \nu_{zr}^{\text{Eff}}$ which can be obtained from the volume averaged strain response from one of the strain increments (i.e. the first time conducting step 2 of the algorithm), or may be calculated a priori using established tools such as the Mori-Tanaka method (Mori and Tanaka, 1973; Benveniste, 1987) for microscale RVEs containing finite aspect ratio CNTs or from the composite cylinders method (Seidel and Lagoudas, 2006) for infinitely long CNTs (i.e. aspect ratios greater than 200^2 (McCullough, 1990)). For the case of plane strain uniaxial tension (i.e. uniaxial tension in the transverse microscale RVE), the nanocomposite gauge factor can be derived from Eq. (2.38) and obtained as³

$$\mathbf{G}^{\text{Eff}} = \frac{1}{\varepsilon_0} \left(\frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} \frac{1 + \varepsilon_0}{1 - \frac{(\nu_{21}^{\text{Eff}} + \nu_{31}^{\text{Eff}} \nu_{23}^{\text{Eff}})\varepsilon_0}{1 - \nu_{22}^{\text{Eff}} \nu_{23}^{\text{Eff}}} - 1 \right)$$
(2.41)

²Micromechanics analysis for fiber reinforced composites with aspect ratios of 200 or greater have been observed to yield effective elastic properties nearly equal to those obtained when using infinitely long (continuous) fibers, even when the differences in elastic properties are 2 to 3 orders of magnitude between the fiber and matrix (McCullough, 1990). However, for the effective electrical properties which have differences in conductivities of more than 14 orders of magnitude, much larger aspect ratios are required to have the same correspondence between the finite aspect ratio and continuous fiber cases, i.e. to be able to ignore end effects, as observed in Ref. (Seidel and Lagoudas, 2009; Seidel and Puydupin-Jamin, 2011) and in here in Fig. 2.8(b) in which the zero strain effective resistivities are plotted as a function of aspect ratio.

³See Appendix B for detailed derivations of the effective gauge factors of the plane-strain tension tests.

Similarly, for the transverse plane strain symmetric biaxial tension case, Eq. (2.38) becomes independent of the effective Poisson's ratios, and is given by

$$\mathbf{G}^{\text{Eff}} = \frac{1}{\varepsilon_0} \left(\frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} - 1 \right) \tag{2.42}$$



Figure 2.4: Schematic representation of the calculation of macroscale gauge factors for a) a general uniaxial tension tension test, b) a uniaxial tension test in the alignment direction of an effectively transversely isotropic nanocomposite, and c) a uniaxial tension test in the transverse direction of an effectively transversely isotropic nanocomposite.

2.3 Results and Discussion

The polymer matrix used in the model is the epoxy resin EPON 828 which is assumed to be isotropic linear elastic below its glass transition temperature. The detailed mechanical, electrical and geometric parameters of the CNT and EPON 828 matrix are listed in Table 2.3: Experimental efforts have demonstrated that the gauge factor of a single metallic SWCNT (G^{C}) can be as high as 2900 (Stampfer et al., 2006), which can thus be used to determine an initial value for the CNT piezoresistive strain coefficient by rearranging Eq. (2.38) as

$$\rho_{zz}^{\rm C}(\varepsilon_{\rm C}) = \rho_{zz}^{\rm C0} ({\rm G}^{\rm C}\varepsilon_{\rm C} + 1) \frac{(1 - \nu_{zr}^{\rm C}\varepsilon_{\rm C})^2}{1 + \varepsilon_{\rm C}}$$
(2.43)

Table 2.3: Mechanical, electrical and geometric parameters for the CNT and EPON 828 polymer matrix (Hammerand et al., 2007; Seidel and Lagoudas, 2009; Ebbesen et al., 1996; Schadler et al., 1998; Arris, 2000). The conductivity of the CNT listed here is the initial conductivity with zero strain.

Properties Materials	Geometry	Mechanical	Electrical	
Single welled CNT	$R_{\text{Out}}=0.85\text{nm}$	E = 1100Gpa	$r = 10^5 S/m$	
Single-wanted Civi	$R_{\rm In}=0.51\rm nm$	v = 0.14	$\kappa = 10 \ S/m$	
EPON 828	$V_{\rm f} = 1 - \tfrac{V_{\rm CNT}}{V_{\rm RVE}}$	E = 3.07 Gpa	$1.40 \times 10^{-9} G/_{\odot}$	
		$\upsilon = 0.3$	$\kappa = 1.49 \times 10^{-5} S/m$	

where it has been understood that the experimental conditions are most reflective of uniaxial tension of the CNT along the CNT axis. Applying the piezoresistive constitutive equation and solving for the axial piezoresistive strain coefficient one obtains

$$g_{zz}^{\rm C}(\varepsilon_{\rm C}) = \frac{1}{\varepsilon_{\rm C}} (\rho_{zz}^{\rm C0} ({\rm G}^{\rm C} \varepsilon_{\rm C} + 1) \frac{(1 - \nu_{z\tau}^{\rm C} \varepsilon_{\rm C})^2}{1 + \varepsilon_{\rm C}} - \rho_{zz}^{\rm C0})$$
(2.44)

Using the data from Table 2.3 and the gauge factor of 2900 and CNT strain value of $\varepsilon_{\rm C} = 1.5\%$ obtained from Ref. (Stampfer et al., 2006), a CNT axial piezoresistive strain coefficient of $g_{zz}^{\rm C} = 2.84\text{E}-2\,\Omega \cdot \text{m}$ is obtained and used along with additional selected values in a parametric study of the piezoresistive response of CNT-polymer nanocomposites the outcomes of which are discussed below.

2.3.1 Nanocomposite Piezoresistive Response Under Uniaxial Tension in the CNT Alignment Direction

The axisymmetric microscale RVE is used to parametrically assess the influence of CNT gauge factor on the macroscale piezoresistive response of nanocomposites in tension in the CNT alignment direction. Five CNT gauge factors are considered, with the first case cor-

responding to the experimentally reported CNT gauge factor. The CNT gauge factors and their corresponding axial piezoresistive strain coefficients are provided in Table 2.4. It is noted that in order to focus on the dominant strain component's impact on piezoresistivity it is assumed that only the axial piezoresistive strain coefficient is non-zero. The evolution

Table 2.4: The conversions from CNT gauge factor to CNT axial piezoresistive strain coefficient g_{zz}^{C} , in which case AU1 is converted at the strain $\varepsilon_{C} = 1.5\%$ as in Ref. (Stampfer et al., 2006), and cases AU2-AU5 are converted at the strain $\varepsilon_{C} = 1\%$. For each case it assumed that all other g_{ij}^{C} are zero.

Case#	$\mathbf{G}^{\mathbf{C}}$	$\mathbf{g}_{zz}^{\mathrm{C}}\left(\boldsymbol{\Omega}\cdot\mathbf{m}\right)$
AU1	2900	2.84E-2
AU2	1E6	9.87E0
AU3	1E11	9.87E5
AU4	1E13	9.87E7
AU5	1E17	9.87E11

of local strains and resistivities under applied macroscale strain increments are provided in Fig. 2.5 for a CNT volume fraction of 0.20 and aspect ratio (AR = $\frac{L_{CNT}}{2r_{Out}}$) of 5 and for a CNT gauge factor corresponding to Case AU1. The contour plots demonstrate the direct correspondence between changes in local strain in the CNT and changes in the local CNT resistivity while the local matrix resistivity remains unchanged despite changes in local strains. Further verification of the piezoresistive implementation within the microscale RVE is obtained by plotting the resistivity as a function of applied boundary strain for an element located in the middle of the CNT as provided in Fig. 2.6. It is observed that the axial resistivity of the CNT element is changing as a linear function of the boundary strain while the conductivity varies as its inverse, and therefore accurately reflects the linear piezoresistive constitutive response of the CNT. Though not present in the axisymmetric uniaxial tension results provided here, it is worth noting that compressive strains of a sufficiently large value for a given CNT piezoresistive strain coefficient can lead to negative values for the conductivity. As such cases are deemed to be not of physical interest herein, tensioncompression asymmetry is introduced into the piezoresistive response such that at a critical compressive strain value, the linear piezoresistive response should smoothly transitions to one which asymptotically approaches zero. For practical simplicity, in the present work a constant small resistivity value is used at the critical compressive strain value and maintained throughout further compressive strains in a manner analogous to a perfectly plastic response in mechanical loading, with the exception being that unloading follows the same path as loading in the piezoresistive case (as opposed to unloading elastically in the mechanical analog). This behavior will play a role in some of the transverse hexagonal microscale RVE cases to be discussed in Section 3.2 for large CNT gauge factors. Having demonstrated successful implementation of the piezorsistive algorithm, the remaining results focus on nanocomposite effective piezoresistive response for CNT having higher aspect ratios (e.g. 50, 100, 200, 300, 1000, 3000 and infinite), and at CNT volume fractions of 0.005, 0.01, 0.05, and 0.10. It is noted that common SWCNT aspect ratios range between 300 to 600, and in some cases to more than 1000. It is also noted that, the vertical separation between the end of the CNT and the boundary of the axisymmetric RVE is set to be consistent with the maximum allowable separation at the CNT aspect ratio of 1 for every given volume fraction. The separation is then held constant for higher aspect ratios so that in the limit case the radius R becomes the one of the infinite case of which the transverse hexagonal RVE is a good approximation⁴.

The influence of the CNT gauge factor on the change in effective axial resistivity component as a function of applied boundary strain, i.e. $\Delta \rho_{zz}^{\text{Eff}} = \rho_{zz}^{\text{Eff}}(\varepsilon_0) - \rho_{zz}^{\text{Eff}}(0)$, is provided in Fig. 2.7. In Fig. 2.7(a) the change in effective axial resistivity of the nanocomposite for Case AU1 (CNT gauge factor of 2900) is observed to behave in an approximately linear fashion with respect to the applied boundary strain up to 1% strain. As such, one could directly determine an effective piezoresistive strain coefficient for the nanocomposite of $g_{zz}^{\text{Eff}} = 4.26 \ \Omega \cdot m$ from

⁴See Appendix C for the geometry correspondence between axial and transverse RVEs.



Figure 2.5: The evolution of local strains and resistivities under applied macroscale strain increments for a CNT volume fraction of 0.20 and aspect ratio of 5 and for a CNT gauge factor corresponding to Case AU1. A potential difference of 1V is applied between the top and bottom edge of the microscale RVE. The results are shown in the form of contour plots of the axial strain component ε_{zz} and axial resistivity component ρ_{zz} in response to the applied homogeneous boundary strain which is linearly increased from 0% to 1%. The volume fraction of the CNT in the microscale RVE is 0.20, with an aspect ratio of 5, which are higher and lower, respectively, than typical CNT-polymer nanocomposite values, but are selected here to better view changes within the CNT.

the slope of the line. However, as the CNT gauge factor is increased, the change in the effective axial resistivity of the nanocomposite as a function of applied boundary strain becomes non-linear, as shown in Fig. 2.7(b) for Case AU4 (CNT gauge factor of 1E13). As this non-linearity is observed at applied strains of less than 1% where the common metallic materials in strain gauges would demonstrate a linear response due strictly to geometry and Poisson's ratio (i.e. $\rho^{f}/\rho^{0} = 1$), the non-linearity is directly attributed to difference in final



Figure 2.6: The change of electrical properties within an element of the CNT in response to the applied boundary strain, ε_0 . The results correspond to an element near the center of the CNT shown in Fig. 2.5, and are therefore reflective of a CNT with AR = 5 and gauge factor of that of Case AU1 at a CNT volume fraction of 0.20.

and initial nanocomposite conductivities. Further, as the CNT piezoresistive constitutive response remains linear throughout the range of applied boundary strains, the nanocomposite non-linearity is therefore associated with the evolution of the local strain fields under the applied load. In Fig. 2.7(c) it is noted, however, that the change in effective nanocomposite conductivity as function of applied boundary strain can reach a saturation limit. This is because, under sufficiently large enough applied strains, the CNT resistivity effectively becomes greater than that of matrix, thereby switching the composite behavior from that of conductive fillers in a non-conducting matrix to a non-conducting matrix with voids. Even though the piezoresistivity of the CNT may lead to CNT resistivities which are very large compared to that of the matrix, as the volume fraction of CNT remains fixed, at the saturation point the matrix essentially only experiences a negligibly better approximation of void from the CNT so that the effective nanocomposite resistivity no longer appreciably increases with increasing applied boundary strain. The larger the CNT gauge factor, the lower the value of applied boundary strain one can expect to achieve saturation. For the Case AU5 (CNT gauge factor of 1E17), the saturation point occurs at an applied boundary strain of approximately 0.05%, after which the percent difference increase of the change of effective resistivity is no higher than 0.1%. It is worth noting, however, that the use of linear



Figure 2.7: Nanocomposite effective axial resistivities ρ_{zz}^{Eff} obtained from the axisymmetric microscale RVE in response to the applied boundary strain ε_0 for a CNT volume fraction of 0.005 and CNT aspect ratio of AR=300. a) Change of the effective resistivity component $\Delta \rho_{zz}^{\text{Eff}}$ as a function of the applied boundary strain of the microscale RVE for Case AU1 with $G^{\text{C}} = 2900$. b) $\Delta \rho_{zz}^{\text{Eff}}$ vs ε_0 for Case AU4 with $G^{\text{C}} = 1\text{E}13$. c) $\Delta \rho_{zz}^{\text{Eff}}$ vs ε_0 for Case AU5 with $G^{\text{C}} = 1\text{E}17$. d) $\Delta \rho_{zz}^{\text{Eff}}$ vs ε_0 in semi-log plot for the five CNT gauge factor cases listed in Table 2.4.

elastic field equations to obtain the local strains means that the effective nanocomposite piezoresistive response, whether linear, non-linear or saturated, is completely reversible upon unloading. Finally, a comparison of all five axisymmetric uniaxial tension test results is provided in Fig. 2.7(d) in terms of the semi-log plot of the difference between final and initial nanocomposite axial resistivity. There it is observed for Cases AU2 and AU3 that the orders of magnitude increases in CNT gauge factor leads to comparable orders of magnitude increases in $\Delta \rho_{zz}^{\text{Eff}}$, whereas Cases AU4 and AU5 demonstrate the saturation effect associated with the effective switch from conductive inclusions to voids such that further increases in CNT gauge factor will have negligible effects on the effective nanocomposite's piezoresistive response.

The effects on the piezoresistive response of the nanocomposite of increasing the aspect ratio of the CNTs at a fixed volume fraction of 0.01 are provided in Fig. 2.8 for CNT aspect ratios of 50, 100, 200, 300, 1000, 3000 and for the infinitely long (i.e. continuous) CNT case for the CNT gauge factor of AU3. In Fig. 2.8(a) the difference in the volume averaged resistivity of the CNT relative to its zero strain value, i.e. $\Delta \rho_{zz}^{\rm C}$, is observed to demonstrate a quickly converging trend, with percent differences relative to the infinitely long CNT response at an applied strain of 1% of -64.8%, -46.6%, and -7.41% for aspect ratios of 50, 100, and 1000, respectively. As all of the CNTs regardless of aspect ratio have the same uniform zero strain resistivity and piezoresistive strain coefficient, the observed differences in $\Delta \rho_{zz}^{C}$ are attributed to the differences in the amount of strain transferred to the CNT, where the infinitely long case directly carries the applied strain while the CNTs with aspect ratios of 50, 100, and 1000 carry volume averaged strains of 35.2%, 53.4%, and 92.6% of the applied strain, respectively. However, unlike the CNT, the nanocomposite effective resistivities at zero strain vary significantly with aspect ratio as shown in Fig 12b. In fact, while the 100 and 1000 aspect ratio cases have zero strain effective resistivities which are 16.2% and 79.2% lower than the aspect ratio of the 50 case, due to the large differences between the zero strain CNT resistivity and that of the matrix, all of the aspect ratios considered here remain orders of magnitude higher (~ 11) than the nanocomposite effective resistivity of the infinitely long case, indicating that significantly larger aspect ratios are needed in order to see the same convergence towards the infinitely long behavior for the effective electrical properties than was observed for the convergence of effective mechanical properties of the nanocomposite. Thus, even though all of the aspect ratios considered demonstrate CNT piezoresistive responses $(\Delta \rho_{zz}^{\rm C})$ which converge over a range of a few orders of magnitude $(10^2 \text{ to } 10^4)$, resulting in the change in nanocomposite effective resistivity $(\Delta \rho_{zz}^{\text{Eff}}(\varepsilon_0))$ also

varying over a range of a few orders of magnitude $(10^4 \text{ to } 10^7)$, it is perhaps more meaningful to consider the change in nanocomposite effective resistivity normalized by the given aspect ratio's zero strain resistivity, i.e. $\Delta \rho_{zz}^{\text{Eff}}(\varepsilon_0) / \rho_{zz}^{\text{Eff}}(0)$ as provided in Fig 2.8(c). From such a representation one can quickly observe two key points. The first is that the aspect ratio strongly influences the sensitivity of the piezoresistive response, with higher aspect ratios demonstrating greater sensitivity, e.g. an aspect ratio of 100 yields a 0.14% increase in resistivity at 1% strain whereas an aspect ratio of 3000 yields a 22.8% increase in resistivity at that same strain level. The second key point observed from the normalized change in resistivity is that sensitivity, like the overall effective resistivity, requires much higher aspect ratios than considered here in order to converge to the infinitely long CNT case which has a sensitivity measured in orders of magnitude at 1% strain. Thus, aspect ratio can be viewed as a tuning parameter for having a desired uniaxial strain sensitivity at a given volume fraction.

The influence of CNT volume fraction on the effective piezoresistive response of the nanocomposite to applied uniaxial strain in the CNT alignment direction is provided in Fig. 2.9 for a fixed CNT aspect ratio of 300 and for CNT gauge factors corresponding to cases AU3 and AU4. As the strains within the CNT vary by only a small amount (<1% with lower volume fractions having larger strains) so that the changes in nanocomposite effective resistivity $(\Delta \rho_{zz}^{\text{Eff}}(\varepsilon_0))$ are all of the same order of magnitude, it is again deemed more informative to observe the zero strain normalized response, i.e. $\Delta \rho_{zz}^{\text{Eff}}(\varepsilon_0)/\rho_{zz}^{\text{Eff}}(0)$. As the zero strain resistivities vary by as much as 88%, with resistivities of 3.91E8 $\Omega \cdot m$, 2.78E8 $\Omega \cdot m$, 8.58E7 $\Omega \cdot m$, and 4.64E7 $\Omega \cdot m$ at volume fractions of 0.005, 0.01, 0.05, and 0.1, respectively, large differences in the sensitivity of the nanocomposite piezoresistive response can be observed, with the higher volume fractions being more sensitive to the applied strain than the lower volume fractions. In Fig. 2.9(a) the CNT gauge factor of $G^{C} = 1E11$ is observed to yield a linear normalized piezoresistive response at all volume fractions considered, with the volume fraction of 0.1 demonstrating much higher sensitivity than the volume fraction of 0.005 by roughly two times. The same trend in terms of higher volume fractions yielding higher sen-



Figure 2.8: The effect of aspect ratio of the CNT on the effective electrical properties of the nanocomposites for a CNT volume fraction of 0.01 and CNT gauge factor of case AU3 ($G^{C} = 1E11$). a) Volume averaged $\Delta \rho_{zz}^{C}(\varepsilon_{0})$ within the CNT vs ε_{0} for different aspect ratios of the CNT. b) The zero strain effective resistivity $\rho_{zz}^{\text{Eff}}(0)$ of the nanocomposites vs aspect ratio of the CNT. c) $\frac{\Delta \rho_{zz}^{\text{Eff}}(\varepsilon_{0})}{\rho_{zz}^{\text{Eff}}(0)}$ vs ε_{0} for different aspect ratios of the CNT.

sitivities is again observed in Fig. 2.9(b) for the CNT gauge factor of $G^{C} = 1E13$, however, the sensitivities are an order of magnitude higher and demonstrate a non linear response as observed in Fig. 2.7(b) for the same CNT strains and zero strain resistivities. It is of interest to note that response for the volume fraction of 0.05 is consistently closer to the 0.1 volume fraction response than it is to the 0.01 volume fraction. While the difference in CNT strains between the 0.05 volume fraction case and the 0.01 and 0.1 volume fraction cases are 0.23% and 0.36%, respectively, the difference in zero strain resistivities between these cases are 224% and 46%, respectively, so that the sensitivity of the 0.05 volume fraction case behaves more like that of the 0.1 volume fraction. This is perhaps best understood from observing a comparison between the results obtained from the axisymmetric finite element



Figure 2.9: The relative change of the effective axial resistivities of the nanocomposites in response to the applied boundary strain ε_0 with 4 different volume fractions of the CNT, which are 0.005, 0.01, 0.05, and 0.1. a) $\frac{\Delta \rho_{zz}^{\text{Eff}}}{\rho_{zz}^{\text{Eff}}(0)} \times 100\%$ vs ε_0 for Case AU3 with $G^{\text{C}} = 1\text{E}11$. b) $\frac{\Delta \rho_{zz}^{\text{Eff}}}{\rho_{zz}^{\text{Eff}}(0)} \times 100\%$ vs ε_0 for Case AU4 with $G^{\text{C}} = 1\text{E}13$. The aspect ratio of the CNT is 300.

model for the infinitely long CNT case with results from composite cylinders model where the CNT resistivity has been modified according to the piezoresistive constitutive equation based on the applied strain and a CNT gauge factor of $G^{C} = 1E11$. Such a comparison in terms of nanocomposite effective axial resistivity versus CNT volume fraction is provided in Fig. 2.10, and demonstrates excellent agreement between the finite element and composite cylinder models at all strain levels and volume fractions. The effective axial conductivity obtained from the composite cylinder model is known to be well-approximated by the rule of mixtures, so that the effective resistivity varies as its inverse so that, as is observed in Fig. 2.10, the higher volume fractions have lower overall resistivities, but greater sensitivities such that the volume fraction of 0.05 results are closer to the 0.1 volume fraction results than to the 0.01. Thus, through a combination of aspect ratio and volume fraction, the piezoresistive response in the axial direction under uniaxial tension can be tailored towards a desired overall resistivity and sensitivity level.

It is observed that with a higher volume fraction of the CNT, the initial effective resistivity is lower and the curve increases more slowly than the ones with a lower volume fraction of the CNT, which behaves different than the results of the transverse piezoresistive response.



Figure 2.10: Comparison between the results obtained from the axisymmetric finite element model for the infinitely long CNT case with results from composite cylinders model where the CNT resistivity has been modified according to the piezoresistive constitutive equation based on the applied strain and a CNT gauge factor of $G^{C} = 1E11$. It is noted that all cases converge to the matrix resistivity of 6.71E8 $\Omega \cdot m$ at a volume fraction of 0, but would lead to different values at a volume fraction of 1 due to the changing resistivity of the CNT with applied strain.

This is because the initial effective resistivity is directly influenced by the volume fraction of the CNT, and with a higher volume fraction the effective resistivity can be lower, on the other hand the slope of the curve is influenced by the strain level within the CNT, and with a higher volume fraction the strains within the CNT are lower, causing the curves increase less rapidly.

By applying Eq. (6.6), one can obtain the effective gauge factors of the nanocomposites, G^{Eff} , under uniaxial tension in the CNT alignment direction. Values for the effective nanocomposite gauge factors are provided in Table 2.5 at volume fractions of 0.005 and 0.01 for CNTs having the five CNT gauge factors considered and aspect ratio of 300. For cases AU1 and

Table 2.5: The effective nanocomposite gauge factors G^{Eff} at strain levels of 0.1%, 0.4% 0.7% and 1.0% for CNT-polymer nanocomposites having CNT volume fractions of 0.005 and 0.01 and CNTs with CNT gauge factors corresponding to cases AU1 through AU5 for a CNT aspect ratio of 300.

		$V_{\rm f} = 0.005$				$V_{\rm f} = 0.01$			
Case	$\varepsilon_0 =$	0.1%	0.4%	0.7%	1%	0.1%	0.4%	0.7%	1%
AU1	$\mathbf{G}^{\mathrm{Eff}}$	1.60	1.60	1.60	1.61	1.60	1.60	1.60	1.61
AU2	$\mathbf{G}^{\mathrm{Eff}}$	1.60	1.60	1.60	1.61	1.60	1.60	1.60	1.61
AU3	$\mathbf{G}^{\mathrm{Eff}}$	2.44	2.44	2.45	2.45	2.74	2.75	2.76	2.76
AU4	$\mathbf{G}^{\mathrm{Eff}}$	76.75	58.84	47.94	40.60	107.54	88.28	75.08	65.47
AU5	$\mathbf{G}^{\mathrm{Eff}}$	719.39	182.05	105.28	74.53	1416.16	357.29	205.97	145.35

AU2 the effective nanocomposite gauge factor is observed to have a constant value of 1.6 up to 1% strain indicating 1) that the piezoresistive response is linear and 2) that the inherent piezoresistivity has not had a significant impact on the effective piezoresistive response of the nanocomposite at these strain levels and volume fractions as 1.6 corresponds to the value that would be obtained by purely geometric considerations, i.e. when $\rho_{33}^{\text{Eff}}(\varepsilon_0) = \rho_{33}^{\text{Eff}}(0)$ in Eq. (6.6). As case AU1 was derived from the currently available data on inherent CNT piezoresistivity, these observations imply that the CNTs must have larger gauge factors if inherent CNT piezoresistivity were to be the driving mechanism behind the observed nanocomposite piezoresistivity, or that additional mechanisms such as CNT network deformation and electron hopping play a much a larger role than inherent CNT piezoresistivity in driving nanocomposite piezoresistivity. In terms of assessing larger CNT gauge factors, it is observed that case AU3, having a CNT gauge factor which is of eight orders larger than case AU1, yields effective nanocomposite gauge factors which retain an approximately linear piezoresistive response at values of 2.4 and 2.7 for volume fractions of 0.005 and 0.01, respectively, which are on the same order as the gauge factor measured in the axial direction
of a nanocomposite made of 0.5% wt MWCNT that aligned by AC electric field which has been reported as 2.78 ± 0.42 (Oliva-Aviles et al., 2011). In contrast, cases AU4 and AU5 demonstrate non-linear effective nanocomposite piezoresistive responses which yield effective nanocomposite gauge factors that are orders of magnitude larger than experimentally reported values, and therefore can be used to set upper bounds on potential CNT gauge factors.

2.3.2 Results for the Transverse Piezoresistive Response of the Nanocomposites

The transverse microscale RVE is used to parametrically assess the influence of CNT inherent piezoresistivity on the macroscale piezoresistive response of nanocomposites in the transverse directions with respect to CNT alignment direction. As noted in the introduction, the majority of data regarding inherent piezoresistivity of CNTs is limited to axial testing. As such, there is little data available regarding the remaining independent piezoresistive strain coefficients needed to fully characterize the transversely isotropic piezoresistive response of the CNT. As such, two reduced sets of CNT piezoresistive strain coefficients in the transverse direction are considered. In the first set the normal strain response are equally weighted in terms of piezoresistive strain coefficients, but are decoupled, i.e. $g_{11}^{C} = g_{22}^{C}$ and $g_{12}^{C} = 0$, while in the second set, normal strain responses are equally weighted and coupled, i.e. $g_{11}^{C} = g_{22}^{C}$ and $g_{12}^{C} = 0$, while in the second set, normal strain responses are equally weighted and coupled, i.e. $g_{11}^{C} = g_{22}^{C} = g_{12}^{C} = g_{12}^{C}$. The initial value for the piezoresistive strain coefficients is taken to be the same value as applied in the axial case, with the parametric study focusing on orders of magnitude increases from this base value as reported in Table 2.6. Both sets of piezoresistive strain coefficients are subjected to transverse uniaxial tension and transverse biaxial tension loadings.

The distributions of local strain and resistivity components of the plane-strain uniaxial tension in the 2-direction test are provided in Fig. 2.11 for a CNT volume fraction of 0.60 and for CNT piezoresistive strain coefficients corresponding to cases T1 and T6, respectively. The contour plots demonstrate the direct correspondence between changes in local strains

Table 2.6: The conversions from CNT gauge factor to CNT piezoresistive strain coefficients, in which cases T1 and T6 are converted at the strain $\varepsilon_{\rm C} = 1.5\%$ as in Ref. (Stampfer et al., 2006), and the remaining cases are converted at the strain $\varepsilon_{\rm C} = 1\%$. For each case, it is assumed that all other $g_{ij}^{\rm C}$ are zero.

Case#	$\mathbf{G}^{\mathbf{C}}$	Piezo coefficients $(\Omega\cdot\mathbf{m})$
T1	2900	$g_{11}^C = g_{22}^C = 2.84E-2$
Τ2	1E8	$g_{11}^C = g_{22}^C = 9.87E2$
T3	1E14	$g_{11}^C = g_{22}^C = 9.87E8$
Τ4	1E17	$g_{11}^C = g_{22}^C = 9.87E11$
T5	1E20	$g_{11}^C = g_{22}^C = 9.87E14$
T6	2900	$g_{11}^C = g_{22}^C = g_{12}^C = 2.84E-2$
Τ7	1E8	$g_{11}^C = g_{22}^C = g_{12}^C = 9.87E2$
Τ8	1E14	$g_{11}^C = g_{22}^C = g_{12}^C = 9.87E8$
Т9	1E17	$g_{11}^{C} = \overline{g_{22}^{C}} = g_{12}^{C} = 9.87E11$
T10	1E20	$g_{11}^{C} = \overline{g_{22}^{C} = g_{12}^{C} = 9.87E14}$

in the CNTs and changes in the local CNT resistivities while the local matrix resistivity remains unchanged despite changes in local strains. In Fig. 2.11(b) one can observe that ρ_{11}^{C} and ρ_{22}^{C} within the CNTs are decoupled and directly correspond to ε_{11} and ε_{22} of the CNTs, respectively, which are provided in Fig. 2.11(a). In contrast, in Fig. 2.11(c) it is observed that under those same strain distributions, ρ_{11}^{C} and ρ_{22}^{C} have identical contours due to the use of the coupling term g_{12}^{C} and its being equal to the values assigned to both g_{11}^{C} and g_{22}^{C} . As mentioned before, tension-compression asymmetry is introduced in the CNT piezoresistive response to avoid having compressive CNT strains sufficiently large so as to induce resistivity components which would be less than zero. The compressive strain cutoff is demonstrated in Fig. 2.12 using an element in compression in ε_{11} obtained from the transverse uniaxial tension loading in the 2-direction for a CNT piezoresistive strain coefficient corresponding to



Figure 2.11: The distribution of local strains and resistivities of the plane-strain uniaxial tension in the 2-direction test at $\varepsilon_0 = 1\%$. a) Distribution of ε_{11} and ε_{22} for cases T1 and T6 at $\varepsilon_0 = 1\%$. b) Distribution of ρ_{11} and ρ_{22} for case T1 at $\varepsilon_0 = 1\%$. c) Distribution of ρ_{11} and ρ_{22} for case T6 at $\varepsilon_0 = 1\%$. The volume fraction of the CNTs in the microscale RVE is 0.60, which is higher than typical CNT-polymer nanocomposite volume fraction, but is selected here to better view changes within the CNTs.

case T1. There it is observed that the resistivity of the CNT initially follows the same linear piezoresistive response as elements in tension up until the point where the subsequent strain increment would lead to a negative resistivity. At this point, the previous strain increment's resistivity value is instead prescribed and maintained for all subsequent compressive loading steps. The behavior is analogous to perfectly plastic response, with the exception being that unloading follows the same path as loading.

Having demonstrated the implementation of the piezoresistive algorithm, the remaining results focus on nanocomposite effective piezoresistive response for CNT having lower volume



Figure 2.12: The CNT resistivity component ρ_{11}^{C} of an element within the CNT in response to local compressive strain component ε_{11} for case T1 of the plane-strain uniaxial tension test as ε_0 in the 2-direction increases from 0% to 1% for a transverse RVE with CNT volume fraction of 0.60.

fractions (e.g. 0.005, 0.01, 0.05, and 0.10). The influence of CNT piezoresistive strain coefficients on the change in effective resistivity component ρ_{22}^{Eff} as a function of applied boundary strain (i.e. $\Delta \rho_{22}^{\text{Eff}} = \rho_{22}^{\text{Eff}}(\varepsilon_0) - \rho_{22}^{\text{Eff}}(0)$) for the plane-strain uniaxial tension in the 2-direction test is provided in Fig. 2.13. In comparing the response in Fig. 2.13(a) to the piezoresistive response of the nanocomposite to uniaxial tension in the axial direction provided in Fig. 2.7(a), one can observe that $\Delta \rho_{22}^{\text{Eff}}$ of the plane-strain uniaxial tension test for cases T1 and T6 are 6 orders smaller than $\Delta \rho_{zz}^{\text{Eff}}$ of the axisymmetric uniaxial tension test for case AU1 having the same $G^{C} = 2900$, and display a slightly non-linear response. Similarly, one can compare the curves in Fig. 2.13(b) for $\Delta \rho_{22}^{\text{Eff}}$ curve in Fig. 2.7(c) for axisymmetric case AU5 having the same $G^{C} = 1E17$ and observe that both T4 and T9 are 2 or more orders of magnitude smaller than AU5. As a result, the transverse uniaxial tension cases have yet to have achieved the saturation limit observed in the axisymmetric uniaxial loading case. Further, in comparing the curves in Fig. 2.13(c) and Fig. 2.13(d) to the curves in Fig. 2.7(d), one can observe that the saturated $\Delta \rho_{22}^{\text{Eff}}$ of the plane-strain uniaxial tension test for cases T4 and T9 to the $\Delta \rho_{zz}^{\text{Eff}}$ curve in Fig. 2.13(d) to the curves in Fig. 2.13(d), one can observe that BO5. As a result, the transverse uniaxial tension cases have yet to have achieved the saturation limit observed in the axisymmetric uniaxial loading case. Further, in comparing the curves in Fig. 2.13(c) and Fig. 2.13(d) to the curves in Fig. 2.7(d), one can observe that the saturated $\Delta \rho_{22}^{\text{Eff}}$ of the plane-strain uniaxial tension test for cases have yet to have achieved the saturation limit observed in the axisymmetric uniaxial loading case. Further, in comparing the curves in Fig. 2.13(c) and Fig. 2.13(d) to the



Figure 2.13: Nanocomposite effective transverse resistivity component $\Delta \rho_{22}^{\text{Eff}}$ obtained from the transverse hexagonal microscale RVE in response to the applied boundary strain ε_0 of the plane-strain uniaxial tension in the 2-direction test, in which the volume fraction of the CNT is 0.005. a) Change of the effective resistivity component $\Delta \rho_{22}^{\text{Eff}}$ as a function of the applied boundary strain of the microscale RVE for cases T1 and T6 with $G^{C} = 2900$. b) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 for cases T4 and T9 with $G^{C} = 1E17$. c) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 in semi-log plot for cases T1-T5. d) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 in semi-log plot for cases T6-T10.

test for cases T5 and T10 with $G^{C} = 1E20$ are still 1 to 2 orders smaller than $\Delta \rho_{zz}^{\text{Eff}}$ for case AU5 with $G^{C} = 1E17$. This is in part because in the axisymmetric uniaxial tension test with AR=300, the CNT can take 78.3% of the applied boundary strain ε_{0} in a volume averaged sense, while in the plane-strain uniaxial tension test the CNTs can only take 0.16% and 0.83% respectively for ε_{11} and ε_{22} , respectively, of the applied boundary strain ε_{0} , and therefore have smaller piezoresistive induced changes in the resistivity of the CNTs. It is also due in part to the well-documented micromechanics observation that the transverse properties in aligned fiber composites are dominated by the matrix properties. For example, in the present work, the zero strain axial effective resistivity, $\rho_{zz}^{\text{Eff}}(0)$, at a volume fraction of 0.005 is 42% below that of the matrix while the zero strain transverse effective resistivity, $\rho_{22}^{\text{Eff}}(0)$, at that same volume fraction is only 1% below that of the matrix, thus indicating that whatever piezoresistive changes are brought in the transverse directions of the CNTs will be more difficult detect than in the axial direction.

In Fig. 2.13(c) and Fig. 2.13(d) one can also observe that $\Delta \rho_{22}^{\text{Eff}}$ of cases T6-T10 are consistently greater than $\Delta \rho_{22}^{\text{Eff}}$ of the corresponding cases T1-T5. This is due to the combination of the selected off-diagonal piezoresistive strain coefficient g_{12}^{C} for cases T6-T10 and the dependence of $\Delta \rho_{22}^{\text{Eff}}$ on both $\Delta \rho_{11}^{\text{C}}$ and $\Delta \rho_{22}^{\text{C}}$ of the CNT. The latter may be understood by considering the annular geometry of the CNT as promoting a conductive hoop path which would be governed by the hoop resistivity, $\rho_{\theta\theta}^{\rm C}$, and which by standard transformation is a combination of both $\rho_{11}^{\rm C}$ and $\rho_{22}^{\rm C}$. From Fig. 2.11(a) it was observed that under the plane strain uniaxial tension in the 2-direction, that a significant portion of the CNT was in compression in ε_{11} and in tension in ε_{22} . This observation is better quantified in Fig. 2.14(a) which provides the volume averaged strain components, i.e. $\langle \varepsilon_{11} \rangle$ and $\langle \varepsilon_{22} \rangle$. As a result, the resistivity distribution within the CNT under the application of the piezoresistive strain coefficients $g_{11}^C = g_{22}^C$ becomes non-uniform and orthotropic for cases T1-T5, with the compressive 1-direction strains leading to reductions in 1-direction resistivities, i.e. negative $\Delta \rho_{11}^{\rm C}$, and the tensile 2-direction strains leading to increases in 2-direction resistivity, i.e. positive $\Delta \rho_{22}^{\rm C}$, as can be seen in the volume averaged CNT resistivities provided for case T1 in Fig. 2.14(b). However, the application of an off-diagonal piezoresistive strain coefficient which is equal to the diagonal coefficients in cases T6-T10 results in a CNT resistivity distribution which is still non-uniform, but is now isotropic, with the much larger tensile strains in the 2-direction resulting in large net increases in CNT resistivity, i.e. positive $\Delta \rho_{11}^{C} = \Delta \rho_{22}^{C}$ As can be seen in Fig. 2.14(b), even though the volume averaged change in CNT resistivity Xiang Ren

Chapter 2

 $\langle \Delta \rho_{22}^{\rm C} \rangle$ for case T1 is 24% greater than that of T6 at 1% strain, the volume averaged change in CNT resistivity $\langle \Delta \rho_{11}^{\rm C} \rangle$ for case T1 is 124% lower than that of T6 so that net effect is a larger $\langle \Delta \rho_{22}^{\rm Eff} \rangle$ for T6 than T1.



Figure 2.14: a) The volume averaged strain components $\langle \varepsilon_{11}^{\rm C} \rangle$ and $\langle \varepsilon_{22}^{\rm C} \rangle$ and b) The volume averaged change of resistivity components $\langle \Delta \rho_{11}^{\rm C} \rangle$ and $\langle \Delta \rho_{22}^{\rm C} \rangle$ of the CNTs in response to the applied boundary strain ε_0 of the plane-strain uniaxial tension in the 2-direction test for cases T1 and T6.

The influence of CNT volume fraction on the effective piezoresistive response of the nanocomposite to the applied strain in the plane-strain uniaxial tension in the 2-direction test is provided in Fig. 2.15 for CNT gauge factors corresponding to cases T8 and T9. Similar to what was observed in the axisymmetric uniaxial tension test, large differences in the sensitivity of the nanocomposite piezoresistive response can be observed, with the higher volume fractions being more sensitive to the applied strain than the lower volume fractions. In Fig. 2.15(a), case T8 is observed to yield a seemingly linear normalized piezoresistive response at all volume fractions considered, with the volume fraction of 0.10 demonstrating much higher sensitivity than the volume fraction of 0.005 by roughly 31.7 times. The same trend in terms of higher volume fractions yielding higher sensitivities is again observed in Fig. 2.15(b) for case T9, however, the sensitivities are 3 orders of magnitude higher than the T8 case and demonstrate a slightly non linear response. However, when compared with the sensitivities

observed in the axial direction, the sensitivities observed in the transverse uniaxial tension test are orders of magnitude smaller even for CNT gauge factors which are orders of magnitude larger and include off-diagonal terms. This is due to the matrix dominance of effective properties in the transverse direction which leads to reduced influence of changes in the CNT and to zero strain resisitivities $\rho_{22}^{\text{Eff}}(0)$ which are much larger than their axial counterparts. It is of interest to note that unlike what was observed in the axisymmetric uniaxial tension test, the difference between the curves for volume fractions of 0.05 and 0.10 is much larger than the difference between the curves for volume fractions of 0.005 and 0.01. It will be seen that this observation can be attributed to the manner in which the effective transverse resistivity increases with increasing effective CNT volume fraction for each strain level starting from a large negative slope at zero strain and approaching zero slope as the strain increases.



Figure 2.15: The relative change of the effective resistivity components ρ_{22}^{Eff} of the nanocomposites in response to the applied boundary strain ε_0 of plane-strain uniaxial tension test for CNT volume fractions of 0.005, 0.01, 0.05, and 0.10. a) $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_{22}^{\text{Eff}}(0)} \times 100\%$ vs ε_0 for case T8 with $G^{\text{C}} = 1\text{E}14$. b) $\frac{\Delta \rho_{22}^{\text{Eff}}}{\rho_{22}^{\text{Eff}}(0)} \times 100\%$ vs ε_0 for case T9 with $G^{\text{C}} = 1\text{E}17$.

The results of the plane-strain biaxial tension test are shown in Fig. 2.16. By comparing with the results of plane-strain uniaxial tension test in Fig. 2.13, one can observe that for cases T1 through T10, the changes in effective resistivity component $\Delta \rho_{22}^{\text{Eff}}$ of the plane-strain biaxial tension test are higher than the plane-strain uniaxial tension test by at most two orders. This is because, in contrast to the plane-strain uniaxial tension test, both the ε_{11} and ε_{22} strain components in the CNT are predominantly tensile, resulting in net increases in both components of CNT resistivity, i.e. both $\langle \Delta \rho_{11}^{\rm C} \rangle$ and $\langle \Delta \rho_{22}^{\rm C} \rangle$ are positive. Again in Fig. 2.16 as was observed in Fig. 2.13, the cases T1-T5 are consistently lower in $\Delta \rho_{22}^{\rm Eff}$ than cases T6-T10. However, this is understood in a more straight forward manner for the symmetric biaxial tension case as the overall tensile strain components in both the 1- and 2-directions results in positive contributions to $\Delta \rho_{11}^{\rm C}$ and $\Delta \rho_{22}^{\rm C}$ from the off-diagonal piezoresistive strain coefficient in cases T6-T10 which are not present in cases T1-T5.

It is noted that for the plane-strain biaxial tension cases the strain field in the CNT is nearly uniform, so that for both the T1-T5 and the T6-T10 cases the resistivity in the CNT remains nearly uniform and isotropic. As such, it is possible to use the volume averaged resistivity of the CNT at the various strain levels in a composite cylinders model and construct a comparison with the finite element results for the change in resistivity with applied strain as provided in Fig. 2.17 for case T9. From Fig. 2.17(a) it is observed that as the strain level increases, the slopes of the resistivity vs volume fraction curves obtained from the composite cylinder model rapidly increase in a non-linear fashion such that there is greater divergence between strain levels with increasing volume fraction. Converting this data into the change in resistivity as function of applied strain and overlaying with the finite element results a very good correspondence is obtained between the two models indicating that the nonlinearity observed in the finite element results is consistent within the micromechanics framework, and therefore applicable to other loading states where tools such as the composite cylinder model cannot be used due to the nonuniformity and material symmetry distribution within the CNT, e.g. the plane-strain uniaxial tension or in-plane shear loadings.

By applying Eq.s (3.15) and (2.42), one can obtain the effective gauge factors of the nanocomposites, G^{Eff} , for the plane-strain uniaxial and biaxial tension tests, respectively, in the transverse directions with respect to the CNT alignment direction. Values for the effective nanocomposite gauge factors are provided in Table 2.7 for a CNT volume fraction of 0.005 for each of the ten CNT gauge factors considered in cases T1-T10. For the plane-strain uniaxial tension test, the effective gauge factors of cases T1-T3 and T6-T8 are observed to have a



Figure 2.16: Nanocomposite effective transverse resistivity component $\Delta \rho_{22}^{\text{Eff}}$ obtained from the transverse hexagonal microscale RVE in response to the applied boundary strain ε_0 of the plane-strain biaxial tension test, in which the volume fraction of the CNT is 0.005. a) Change of the effective resistivity component $\Delta \rho_{22}^{\text{Eff}}$ as a function of the applied boundary strain of the microscale RVE for cases T1 and T6 with $G^{\text{C}} = 2900$. b) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 for cases T4 and T9 with $G^{\text{C}} = 1\text{E}17$. c) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 in semi-log plot for the cases T1-T5. d) $\Delta \rho_{22}^{\text{Eff}}$ vs ε_0 in semi-log plot for the cases T6-T10.

constant value of 1.43 up to 1% strain indicating 1) that the piezoresistive response is linear and 2) that the inherent piezoresistivity has not had a significant impact on the effective piezoresistive response of the nanocomposite at these strain levels and volume fractions as 1.43 corresponds to the value that would be obtained by purely geometric considerations, i.e. when $\rho_{22}^{\text{Eff}}(\varepsilon_0) = \rho_{22}^{\text{Eff}}(0)$ in Eq. (3.15). The same conclusions can be drawn for cases



Figure 2.17: Comparison between the results obtained from finite element model with results from composite cylinder model for case T9 of the plane-strain biaxial tension test, where in the CCM model the CNT transverse resistivity has been modified to the volume averaged resistivity based on applied strains on the CNT. a) The effective resistivity component ρ_{22}^{Eff} obtained from CCM model with change of CNT volume fraction at applied boundary strain levels of 0.0%, 0.2%, 0.4%, 0.6%, 0.8%, and 1.0% respectively. b) Comparison between $\Delta \rho_{22}^{\text{Eff}}$ of CCM with $\Delta \rho_{22}^{\text{Eff}}$ of FEM at CNT volume fractions of 0.005, 0.01, 0.05, and 0.10 respectively.

T1-T3 and T6-T8 of the plane-strain biaxial tension test, with an exception being that the effective gauge factors are small enough to be considered 0. This is because, as indicated in Eq. (2.42), the effective gauge factors of the plane-strain biaxial tension test do not rely on geometric effects, but instead depend purely on how the inherent piezoresistivities of CNTs govern the ratio of the effective resistivity to the zero strain effective resistivity. Only when the CNT gauge factor becomes very large as in cases T4-T5 and T9-T10 does the inherent piezoresistivity become a significant influence on the transverse effective nanocomposite gauge factors, doing so in a nonlinear fashion. As case T1 was related to the currently available data on inherent CNT piezoresistivity, these observations imply that the CNTs must have larger gauge factors if inherent CNT piezoresistivity, or that additional mechanisms such as CNT network deformation and electron hopping play a much larger role than inherent

CNT piezoresistivity in driving transverse nanocomposite piezoresistivity. Further, these other mechanisms must have a substantial impact on the change in effective transverse resistivity with applied strain if they are to have a noticeable effect on the transverse effective nanocomposite gauge factor. Thus, in terms of deformation sensing, it is believed that SHM applications should focus on tailoring the gauge factor in the alignment direction of aligned CNT-polymer nanocomposites.

Table 2.7: The effective nanocomposite gauge factors G^{Eff} at strain levels of 0.1%, 0.4%, 0.7%, and 1.0% of the plane-strain uniaxial and biaxial tension tests for CNT-polymer nanocomposites having CNT volume fractions of 0.005 and CNTs with CNT gauge factors corresponding to cases T1 through T10.

		Plane-strain uniaxial tension test		Plane-strain biaxial tension test					
Case	$\varepsilon_0 =$	0.1%	0.4%	0.7%	1%	0.1%	0.4%	0.7%	1%
T1	$\mathbf{G}^{\mathrm{Eff}}$	1.43	1.43	1.43	1.43	1E-14	1E-14	1E-14	1E-14
T2	$\mathbf{G}^{\mathrm{Eff}}$	1.43	1.43	1.43	1.43	1E-9	1E-9	1E-9	1E-9
T3	$\mathbf{G}^{\mathrm{Eff}}$	1.43	1.43	1.43	1.43	1E-3	1E-3	1E-3	1E-3
Τ4	$\mathbf{G}^{\mathrm{Eff}}$	1.43	1.43	1.44	1.44	0.95	0.83	0.74	0.66
T5	$\mathbf{G}^{\mathrm{Eff}}$	2.08	1.62	1.54	1.51	19.69	5.00	2.87	2.01
Т6	$\mathbf{G}^{\mathrm{Eff}}$	1.43	1.43	1.43	1.43	2E-14	2E-14	2E-14	2E-14
Τ7	$\mathbf{G}^{\mathrm{Eff}}$	1.43	1.43	1.43	1.43	2E-9	2E-9	2E-9	2E-9
Т8	$\mathbf{G}^{\mathrm{Eff}}$	1.43	1.43	1.43	1.43	2E-3	2E-3	2E-3	2E-3
Т9	$\mathbf{G}^{\mathrm{Eff}}$	1.70	1.70	1.68	1.68	1.57	1.56	1.56	1.56
T10	$\mathbf{G}^{\mathrm{Eff}}$	18.10	5.83	3.98	3.23	19.86	5.01	2.87	2.01

2.4 Conclusions

Computational micromechanics models are constructed to assess the piezoresistive responses of aligned CNT-polymer nanocomposites in the axial and transverse directions due to the inherent piezoresistivities of CNTs, which are assumed to be well dispersed, and perfectly bonded to the surrounding polymer. A parametric study in terms of CNT gauge factor, aspect ratio, and volume fraction is undertaken to study the influence of these factors on the effective nanocomposite piezoresistive response and gauge factors under uniaxial loading in the axial and transverse directions and symmetric biaxial tension in the transverse direction. The results of the axisymmetric piezoresistive model show that through a combination of aspect ratio and volume fraction, the piezoresistive response in the axial direction under uniaxial tension can be tailored towards a desired overall resistivity and sensitivity level. The obtained effective axial gauge factors suggest that in order for the macroscale axial piezoresistive response of the nanocomposites to be comparable with the experimental results in the literature, that very large CNT gauge factors are needed (e.g. 1E11 in case AU3), several orders of magnitude larger than the the maximum CNT gauge factors currently reported in the literature (i.e., ~ 2900). In the transverse direction still larger CNT gauge factors are needed for the inherent piezoresistivity mechanism to have a noticeable effect on the nanocomposite gauge factors in the transverse directions as the electrostatic interactions in the transverse direction are strongly governed by the matrix material. Therefore the analysis implies that either larger CNT gauge factors (in the neighborhood of 1E11 in the axial direction; in the neighborhood of 1E17 in the transverse directions) would be required if inherent CNT piezoresistivity were the principal mechanism driving the observed nanocomposite piezoresistivity, or that the piezoresistive response of the CNT-polymer nanocomposites is due to some additional mechanisms, e.g. electrical tunnelling effect or contact resistance between two adjacent CNTs. Further, these other mechanisms must have a substantial impact on the change in effective resistivity with applied strain, particularly if they are to have a noticeable effect on the transverse effective nanocomposite gauge factor. Thus, in terms of deformation

sensing, it is believed that SHM applications should focus on tailoring the gauge factor in the alignment direction of aligned CNT-polymer nanocomposites by controlling CNT aspect ratio, dispersion and volume fraction to maximize the influence of inherent CNT piezoresistivity in conjunction with tunnelling and contact resistance effects.

Computational Micromechanics Modeling of Piezoresistivity in CNT-Polymer Nanocomposites

3.1 Introduction

Currently several mechanisms, which may potentially account for the observed overall piezoresistivity of the nanocomposites, have been identified. For example, the electrical tunneling effect is a phenomena that when the CNTs are close enough to each other, conducting paths can be formed in the insulating polymer matrix for the electrons to be transported from one CNT to another (Simmons, 1963; Fuhrer et al., 2000; Budlum and Lu, 2001; Li et al., 2007; Xia and Curtin, 2007; Li and Chou, 2008; Li et al., 2008; Theodosiou and Saravanos, 2010; Hu et al., 2012). The electrical tunneling effect has been observed to be highly sensitive to the distances of adjacent CNTs. When distance between two neighboring CNTs is increased by several nanometers, the electrical conductivity in the conductive path between the two CNTs corresponding to electron tunneling is sharply reduced, returning to the insulating

matrix value at the maximum electrical tunneling distance.

In this study, a computational micromechanics model based on finite element analysis is developed and used to determine the relative changes in macroscale resistance (i.e. effective macroscale piezoresistivity) due to changes at the microscale and due to changes of macroscale geometry. Specifically, the microscale mechanisms include the electrical tunneling effect and the coupled effect of electrical tunneling and inherent piezoresistivity of the CNT. The FEM based computational micromechanics approach explicitly accounts for material deformation while tracking CNT relative displacements for electrical tunneling model. Such a approach is able to capture not only this but other deformation based mechanisms affecting the gauge factor such as inherent CNT resistivity and geometry. By varying the volume fraction of the CNT and the height of barrier of the polymer matrix, their influence on the overall piezoresistivity of the nanocomposites is systematically studied. Some initial simulations on the RVE with random aligned CNTs are also conducted and compared with the ones with well-dispersed and aligned CNTs.

3.2 Model Description

We have selected a multiscale idealization as shown in Fig. 3.1, in which the CNTs are assumed to be aligned and perfectly bonded to the surrounding polymer in the microscale. The solution of the macroscale boundary value problem (BVP) is obtained by solving the microscale BVP with periodic boundary conditions applied to the microscale RVEs, as seen in Fig. 3.2. Under in-plane strain assumption consistent with high aspect ratio fibers, the regular hexagonal array RVE as in Fig. 3.2a is used for the case in which there are welldispersed and aligned CNTs, and the RVE as in Fig. 3.2b is used for the case in which there are aligned but randomly distributed CNTs in the transverse plane. The annulus areas represent the cross-sections of CNTs, and the remaining area is pure polymer matrix. Correspondingly, a plane strain periodic finite element model is constructed to model the

piezoresistive response of the nanocomposites in the transverse directions. In order to assess the CNT end effects on the axial effective electrical conductivity, a finite aspect axisymmetric RVE (Fig. 2c) is considered. It is noted that the geometry of the axisymmetric RVE is selected such that as the aspect ratio goes to infinity, that the transverse RVE dimensions in Fig. 2a are obtained as indicated in Ref. (Ren and Seidel, 2013a).



Figure 3.1: The hierarchical multiscale modeling of nanocomposites in which there are aligned CNTs

Boundary conditions applied to the microscale RVEs are selected so as to correspond to uniform strain states in the homogeneous macroscale material BVP as described in Ref. (Ren and Seidel, 2013a) for both the mechanical and electrostatic loadings. Thus, the focus is on solving the microscale mechanical and electrostatic boundary value problems in an appropriately coupled fashion so as to capture the influence of both the electrical tunneling and inherent CNT piezoresistivity mechanisms acting within the microscale RVE.

3.2.1 Mechanical Governing Differential Equations for the Microscale RVE

Under the plane strain assumptions for the transverse hexagonal RVE $\varepsilon_{13} = 0$, $\varepsilon_{23} = 0$, and $\varepsilon_{33} = 0$. At the microscale, the CNT annulus and polymer matrix can be assumed to be



Figure 3.2: Microscale RVEs for the nanocomposites with 10% CNTs. a) is the transverse hexagonal microscale RVE for the well-dispersed and aligned CNTs. b) is the transverse microscale RVE for the aligned CNTs with random in-plane distribution, in which $W_2 = H_2$. c) is the axisymmetric microscale RVE, in which W'_1 goes to $\frac{\sqrt{3}W_1}{6}$ as the aspect ratio of the CNT $A = \frac{L_{CNT}}{2r_{CNT}}$ goes to infinity. ($\frac{\sqrt{3}W_1}{6}$ is the half distance between two adjacent CNTs in a)). Note that the aspect ratio used here is 20, which is only for demonstration purposes as the real aspect ratio used in the computations is much higher.

isotropic linear elastic materials (Saito et al., 1998) such that their constitutive relationships can be denoted with the Lame constants as

$$\sigma_{ij} = 2\mu^{\mathrm{J}}\varepsilon_{ij} + \lambda^{\mathrm{J}}\varepsilon_{kk}\delta_{ij} \tag{3.1}$$

where the superscript J takes values of C or M to denote the elastic constants of the CNT and matrix, respectively, and where the standard relationships $\mu = \frac{E}{2(1+\nu)}$ and $\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}$ hold. The boundary conditions on the microscale RVE can be expressed as displacement boundary conditions by

$$u_i = x_j \tilde{\varepsilon}_{ij}(X_k) \tag{3.2}$$

such that in general the macroscale and microscale RVE strains can be related to one another through microscale volume averages as

$$\tilde{\varepsilon}_{ij}(\dot{X}_k) = \langle \varepsilon_{ij} \rangle \tag{3.3}$$

56

where $\tilde{\varepsilon}_{ij}(\tilde{X}_k)$ are the macroscale strain at a macroscale material point \tilde{X}_k which the microscale RVE represents. The microscale equations expressed here in cartesian coordinates for the plane strain transverse RVEs are suitably represented in cylindrical coordinates for use in the axisymmetric axial RVEs as discussed in Ref. (Ren and Seidel, 2013a).

3.2.2 Electrostatic Governing Differential Equations for the Microscale RVEs

The steady-state conservation of charge equation for the microscale RVE can be denoted in Cartesian coordinates as:

$$J_{i,i} = 0 \tag{3.4}$$

where J_i is the current density, and where under in-plane electrostatic assumptions $J_{3,3} = 0$. The microscale RVE electric field is obtained as the negative of the gradient of the microscale potential as

$$E_i = -\Phi_{,i} \tag{3.5}$$

where E_i (i = 1, 2, 3) and Φ are the electric field and electric potential respectively as applied in Cartesian coordinate system at the microscale and where under in-plane electrostatic assumptions it is noted that $E_3 = 0$. For the microscale RVEs, Ohm's law can be written as

$$E_i = \rho_{ij}^{\rm C}(\varepsilon_{ij}^{\rm C})J_j \tag{3.6a}$$

$$E_i = \rho_{ij}^{\mathrm{M}}(d)J_j \tag{3.6b}$$

where the superscripts C and M on the resistivities denote CNT and polymer matrix respectively. It is noted that the resistivity tensor of the CNT is dependent on the strain field in the CNT due to the inherent piezoresistive effect, and that the resistivity tensor of the polymer matrix is related to the distance (d) between adjacent CNTs in accounting for the electrical tunneling effect. As such, both the CNT and matrix resistivities evolve with the local microscale deformation under the applied macroscale boundary conditions leading to a Xiang Ren

Chapter 3

one-way coupled effective piezoresistive response. The electrical boundary conditions on the microscale RVEs can be expressed as potential conditions by

$$\Phi = x_i \tilde{\mathcal{E}}_i(\tilde{X}_k) \tag{3.7}$$

such that in general the macroscale and microscale RVE electric fields can be related to one another through microscale volume averages as

$$\tilde{E}_i(\tilde{X}_k) = \langle E_i \rangle \tag{3.8}$$

where $\tilde{E}_i(\tilde{X}_k)$ are the macroscale current density and electric field at a macroscale material point \tilde{X}_k which the microscale RVE represents. The microscale equations expressed here in cartesian coordinates for the plane strain transverse RVEs are suitably represented in cylindrical coordinates for use in the axisymmetric axial RVEs as discussed in Ref. (Ren and Seidel, 2013a).

Governing Equations for the Electrical Tunneling Effect in the Polymer Matrix

According to (Simmons, 1963; Hu et al., 2012), the tunneling resistance between two adjacent CNTs can be approximated as

$$R_{\text{tunnel}} = \frac{\Delta V}{AJ} = \frac{h^2 d}{A e^2 \sqrt{2m\lambda}} exp(\frac{4\pi d}{h} \sqrt{2m\lambda})$$
(3.9)

where ΔV is the electrical potential difference, A is the cross-section area of the tunnel, J is the tunneling current density, h is Planck's constant, d is the distance between adjacent CNTs, e is the electric charge, m is the mass of electron, and λ is the height of barrier of the polymer matrix (e.g. for epoxy, $\lambda = 0.5 - 2.5$ eV (Hu et al., 2010, 2012)). The tunneling resistivity ρ_{tunnel} and tunneling resistance can be related through the CNT distance and the cross-sectional area of the tunnel by

$$R_{\rm tunnel} = \rho_{\rm tunnel} \frac{d}{A} \tag{3.10}$$

Xiang Ren

Chapter 3

in which ρ_{tunnel} is defined as the tunneling resistivity, so that upon substitution of Eqn. (3.9), the tunneling resistivity is expressed as

$$\rho_{\text{tunnel}} = \frac{h^2}{e^2 \sqrt{2m\lambda}} exp(\frac{4\pi d}{h} \sqrt{2m\lambda}) \tag{3.11}$$

The advantage of using the tunneling resistivity instead of the tunneling resistance is that we do not need to estimate the cross sectional area of the 'tunnel' when constructing RVEs and their corresponding finite element meshes, nor is the 'tunnel' required to be of uniform cross section. It is further noted that Eq. (7.6) indicates that the electrical tunneling resistivity strongly depends on two variables: the distance between two adjacent CNTs (d) and the height of barrier of the polymer matrix (λ). Fig. 3.3(a) provides a map of constant tunneling resistivities in the two parameter separation distance-barrier height space. It is noted that as the barrier height decreases the corresponding separation distance grows asymptotically whereas when the barrier height increases, the corresponding separation distance asymptotically approaches zero. It is further noted that the tunneling resistivity between adjacent CNTs should not become larger than the original matrix resistivity, in this case, a value of 1E14 as denoted by the dashed line in Fig. 3.3(a). Thus, for a given barrier height and limit matrix resistivity value, the maximum electrical tunneling distance, i.e the cut off distance for electrical tunneling, is set. For example, as observed in Fig. 3.3(b), if we choose a barrier height of $\lambda = 1.5$ eV, as the separation distance between adjacent CNTs increases from 0nm to 2nm, the tunneling resistivity can exponentially increase from the level of a conductor $(10^{-5} \ \Omega \cdot m)$ to the level of an insulator $(10^6 \ \Omega \cdot m)$, and continuing to increase up to a distance of d = 3.14nm where the matrix resistivity is obtained. For a barrier height of λ = 2.5 eV, the resistivity transitions from conductor to insulating matrix more rapidly with a corresponding maximum tunneling distance of 2.66nm, while for barrier height $\lambda = 0.5$ eV, the transition proceeds at slower rate corresponding to a maximum tunneling distance of 5.83nm. For a specific polymer and a specific height of barrier λ , the corresponding distance (d) that recovers the resistivity of the pristine polymer matrix is defined as the maximum or cut off distance d_c for the electrical tunneling effect. It is observed in Fig. 3.3(a) that as λ increases from 0.01 eV to 0.5 eV, d_c decreases in a relatively large scale, which is from

39.33nm to 5.83nm. However, when λ increases from 0.5 eV to 5 eV, d_c decreases in a relatively small scale, which is from 5.83nm to 1.89nm. These cut off distances play a key role in determining whether or not a given volume fraction, having a specified unstrained separation distance between CNTs, corresponds to a percolated state, i.e. if d \leq d_c so that electrical tunneling is occurring. Further, in setting d_c, the barrier height sets the increment at which deformations which bring CNTs closer together or further apart will change the tunneling resistivity, and hence, has a strong influence on the corresponding macroscale piezoresistive response.



Figure 3.3: a) The map of constant tunneling resistivities ρ_{tunnel} in the space of separation distance d and barrier height λ . b) The semi-log plot of the electrical tunneling resistivity ρ_{tunnel} with increase of separation distance d as λ is kept at 0.5 eV, 1.5 eV, and 2.5 eV respectively. The inset is the one in non semi-log plot.

For any point with the matrix material, which for our 2D finite element meshes will correspond to the gauss point(s) of an element, the distances to nearest neighbor CNTs are used to construct the local measure of separation distance (d) to be applied in Eqn. (3.10) along with the selected barrier height in determining the matrix element's local resistivity. For example, for point 1 in Fig. 3.4(a) which lies between adjacent CNTs C1 and C2, the connecting path is straight forwardly identified as $d_1 = d_{1c1} + d_{1c2}$ where d_{1c1} is the distance from point 1 to CNT C1 and d_{1c2} is the distance from point 1 to CNT C2. For point 2, however, which lies between CNTs C1, C2, and C3, the determination of the local element resistivity is obtained by choosing the path of least resistance for the tunneling among three possible paths, i.e. $d_2 = \min(d_{2c1} + d_{2c2}, d_{2c1} + d_{2c3}, d_{2c2} + d_{2c3})$. It is further noted that, in being consistent with notion of the RVE being periodic, that tunneling paths between neighboring RVEs must be accounted for. This is accomplished through the use of ghost CNTs in the neighboring RVEs. For example, for point 3 in Fig. 3.4(a), the local resistivity is obtained from the tunneling distance of $d_3 = d_{3c1} + d_{3c8}$, where C8 is the location of the ghost CNT of the neighboring RVE.

Applying this algorithm to all matrix points in the well-dispersed transverse RVE (Fig. 3.4(b)) leads to clearly visible pattern of tunneling paths within the matrix for percolated volume fractions. The algorithm is likewise applied to a randomly dispersed transverse RVE (Fig. 3.4(c)) and to axisymmetric axial RVE (Fig. 4d). For the randomly dispersed transverse RVE which is noted to be at the same volume fraction as the well-dispersed transverse RVE, it is noted that the dispersion is such that not all neighboring CNTs form tunneling paths, so that there are torturous tunneling paths spanning the RVE and simultaneously pockets of matrix resistivity where no tunneling is taking place. For the axisymmetric axial RVE, it is noted that there is a very strong tunneling effect between the ends of the CNT and ghost CNTs above and below as compared to the transverse tunneling to the surrounding ghost CNTs.

As a result of the applied periodic boundary conditions on the microscale RVE, the local distances between CNTs will change. As such, the algorithm for determining the local



Figure 3.4: a) The schematic illustration of the algorithm for obtaining the electrical tunneling resistivities in the polymer matrix. b)The contour distribution of isotropic resistivity in the hexagonal microscale RVE. c) The contour distribution of isotropic resistivity in the microscale RVE in which there are in-plane random aligned CNTs. d) The contour distribution of isotropic resistivity in the axisymmetric microscale RVE. Note that as the aspect ratio of the CNT is chosen to be 300, the RVE shown here is the zoomed in region focusing on the tip of the axisymmetric RVE. In b), c) and d), the volume percentages of the CNT are chosen to be the same of 10%vol, and the polymer matrixes are also chosen to be the same, i.e. the original resistivity is $10^{14}\Omega \cdot m$ and the height of barrier $\lambda = 0.75$ eV, and the corresponding cut-off distance $d_c = 4.78$ nm.

resistivity due to the tunneling effect must be undertaken at each load step in order to allow the microstructure to evolve according to Eq. (7.6). In some instances, new or lower

resistivity tunneling paths will be formed as CNTs come closer together, while as CNTs move further apart, tunneling paths may become more resistive or be completely disrupted as the distance exceeds d_c . These observations will have a strong influence on the observed effective piezoresistive response of the nanocomposites.

Governing Equations for the Inherent Piezoresistivity of the CNT

The CNTs are expected to exhibit inherent piezoresistivity such that the instantaneous resistivity, $\rho_{ij}^{\rm C}$ is a function of the local strain state within the CNT and can therefore be written as

$$\rho_{ij}^{\mathcal{C}} = \rho_{ij}^{\mathcal{C}0} + \Delta \rho_{ij}^{\mathcal{C}} \tag{3.12}$$

in which ρ_{ij}^{C0} are the initial zero strain resistivities of the CNT, and $\Delta \rho_{ij}^{C}$ are the change in resistivities induced by inherent piezoresistive effect of the CNT. The change in resistivity is related to the strain in the CNT through the piezoresistive strain coefficients as

$$\Delta \rho_{ij}^{\rm C} = \mathbf{g}_{ijkl}^{\rm C} \varepsilon_{kl} \tag{3.13}$$

Material symmetry implications and observations allowing the piezoresistive strain coefficients to be represented in a transversely isotropic form in Voigt notation are provided in Ref. (Ren and Seidel, 2013a). Here, for simplified demonstration purposes, it is further assumed that $g_{1111} = g_{2222} = G_c$ with all other g_{ijkl} being zero.

As a result of the applied periodic boundary conditions on the microscale RVE, the amount of strain transferred to the CNTs will increase, especially at higher volume fractions. The corresponding change in CNT resistivity due to inherent piezoresistivity of the CNT will in turn have influence on the observed effective piezoresistive response of the nanocomposites.

3.2.3 Boundary Conditions and Effective Properties

In the present work, periodic displacement boundary conditions consistent with certain desired uniform macroscale strain states are applied to the microscale RVEs. The uniform

Xiang Ren

Chapter 3

strain fields chosen here are consistent with those present in the macroscale plane-strain uniaxial tension test.



Figure 3.5: Schematic representation of the calculation of macroscale gauge factors for a) a uniaxial tension test in the transverse directions of the nanocomposite specimen with aligned CNTs and b) an axial tension test in the alignment direction of an effectively transversely isotropic nanocomposite.

Herein the focus is on the piezoresistive effect, thus the choice of specific tests are to demonstrate the magnitude of the impact of the strain state on the effective piezoresistive response (e.g. gauge factor) of the nanocomposite material in a manner analogous to experimental characterization efforts (Ren and Seidel, 2013a). The detailed periodic mechanical boundary conditions are listed in Table 3.1. The strain ε_0 corresponds to the strain on a macroscale material point under tension, and is quasi-statically increased within the linear elastic range. The effective properties as noted in Table 3.1 can come from CCM (Seidel and Lagoudas, 2006), Mori-Tanaka (Mori and Tanaka, 1973; Benveniste, 1987) or FEM energy equivalencies (Hammerand et al., 2007) and are dependent only on the volume fraction, they do not evolve with applied strain like the electrical properties do since the mechanical microstructure is static.

In an analogous manner as in the mechanical problem, the macroscale material's effective electrostatic material properties can be obtained by constructing electrical energy equivalence between the microscale RVE and the effective one with homogeneous periodic electrical

Table 3.1: Boundary conditions for the 2D microscale RVEs as shown in Fig. 3.2a, Fig. 3.2b, and Fig. 3.2c.

Type of test	B.C.s
Transverse plane-strain uniaxial	$u_1(\frac{W_1}{2}, X_2) - u_1(-\frac{W_1}{2}, X_2) = -\nu'_{21}\varepsilon_0 W_1^{a}$
tension test	$u_2(\frac{W_1}{2}, X_2) - u_2(-\frac{W_1}{2}, X_2) = 0$
	$u_1(X_1, \frac{W_2}{2}) - u_1(X_1, -\frac{W_2}{2}) = 0$
	$u_2(X_1, \frac{W_2}{2}) - u_2(X_1, -\frac{W_2}{2}) = \varepsilon_0 W_2$
Axial tension test for the	$t_r(\mathbf{R}, X_\mathbf{z}) = t_z(\mathbf{R}, X_\mathbf{z}) = 0$
axisymmetric microscale RVE of	
Fig. 3.2c	$u_r(X_r, \frac{\mathbf{L}}{2}) - u_r(X_r, -\frac{\mathbf{L}}{2}) = 0$
	$u_z(X_{\mathbf{r}}, \frac{\mathbf{L}}{2}) - u_z(X_{\mathbf{r}}, -\frac{\mathbf{L}}{2}) = \varepsilon_0 \mathbf{L}$

^a $\nu_{21}' = \frac{\nu_{21}^{\text{eff}} + \nu_{31}^{\text{eff}} \nu_{23}^{\text{eff}}}{1 - \nu_{32}^{\text{eff}} \nu_{23}^{\text{eff}}}.$

boundary conditions applied. In the present work, periodic potential boundary conditions consistent with certain desired uniform electric field states are applied to the microscale RVEs, as listed in Table 3.2 (Ren and Seidel, 2013a). In general, the electrical resistivities can be obtained from the electrical energy equivalency between the microstructural representation (i.e. the RVE) and an effective homogeneous material having the same exterior geometry and boundary conditions. The equivalency can be expressed as

$$\langle J_i E_i \rangle = \langle W^{\text{RVE}} \rangle = \langle W^{\text{eff}} \rangle = \langle J_i^{\text{eff}} E_i^{\text{eff}} \rangle = \langle \rho_{ij}^{\text{eff}} J_i^{\text{eff}} J_j^{\text{eff}} \rangle$$
(3.14)

where J_i^{eff} and E_i^{eff} denote the current density and electric field in the homogenous material representation. While it can be shown that ρ_{ij}^{eff} obtained in this manner under the assumptions of linear material behavior and perfectly connected phases within the microstructure is independent of the electric fields associated with the applied potentials, i.e. of \tilde{E}_0 , it must be noted however, that due to the electrical tunneling effect in the polymer matrix and the

Xiang Ren

$Chapter \ 3$

Table 3.2: Electrostatic boundary conditions for obtaining the effective electrical conductivities of the 2D microscale RVEs as shown in Fig. 3.2a, Fig. 3.2b, and Fig. 3.2c. Note that κ_{ij}^{eff} are effective conductivities, which can be inversed to obtain the effective resistivities ρ_{ij}^{eff} .

Type of test	B.C.s
For obtaining κ_{11}^{eff}	$\Phi(X_1, \frac{W_2}{2}) - \Phi(X_1, -\frac{W_2}{2}) = 0$
	$\Phi(\frac{W_1}{2}, X_2) - \Phi(-\frac{W_1}{2}, X_2) = E_0 W_1$
For obtaining κ_{22}^{eff}	$\Phi(X_1, \frac{W_2}{2}) - \Phi(X_1, -\frac{W_2}{2}) = E_0 W_2$
	$\Phi(\frac{W_1}{2}, X_2) - \Phi(-\frac{W_1}{2}, X_2) = 0$
For obtaining κ_{12}^{eff}	$\Phi(\frac{W_1}{2}, X_2) - \Phi(-\frac{W_1}{2}, X_2) = E_0 W_1$
	$\Phi(X_1, \frac{W_2}{2}) - \Phi(X_1, -\frac{W_2}{2}) = E_0 W_2$
For obtaining κ_{zz}^{Eff} (κ_{33}^{Eff}) in the	$\Phi(X_{\mathrm{r}}, \frac{\mathrm{L}}{2}) - \Phi(X_{\mathrm{r}}, -\frac{\mathrm{L}}{2}) = \mathrm{E}_{0}\mathrm{L}$
axisymmetric microscale RVE	$\mathbf{J}_r(\mathbf{R}, X_z) = 0$

inherent piezoresistivity of the CNTs, the electronic microstructure is evolving so that the effective resistivity is a function of the relative distances of the CNT and the strains in the CNT, i.e. $\rho_{ij}^{\text{eff}} = \rho_{ij}^{\text{eff}}(\mathbf{d}, \varepsilon_{kl}^{\text{C}})$, and therefore, unlike the effective mechanical properties, must be calculated at each mechanical load increment.

3.2.4 Piezoresistive Algorithm

An incremental algorithm for determining the piezoresistive response of the nanocomposites is developed within a finite element framework, and is applied to the 2D microscale RVEs as shown in Fig. 3.2. The Galerkin method is used to formulate the in-plane finite element models, and the linear triangular elements are used. The mechanical and electrostatic finite element formulations are coupled together sequentially with the mechanical formulation used to first obtain the strains in the microscale RVEs which are then used as inputs for the

electrostatic formulation¹. In step 1 of the algorithm, the electrostatic potential boundary value problems as identified in Table 3.2 are applied to the initial undeformed microscale RVEs, and the electrical energy equivalence is used to obtain the zero-strain resistivities, $\rho_{ij}^{\text{eff}}(0)$, of the microscale RVEs from which the zero strain resistance $\mathbf{R}^{\text{eff}}(0)$ is calculated. In step 2, the first mechanical load increment is applied to the microscale RVEs according to the boundary conditions identified in Table 3.1, resulting in the change relative distances of the CNT and the local strain distributions in the CNT. In step 3, the relative distances of the CNT and the local strains in the CNT obtained from step 2 are used to update local resistivities of the polymer matrix and the CNT. In step 4, the same electrostatic potential boundary value problems from step 1 are applied again to the microscale RVEs with updated local electrical properties of the polymer matrix and the CNT, with the electrical energy equivalency enforced to obtain the effective conductivities $\rho_{ij}^{\text{eff}}(d, \varepsilon_{kl}^{\text{C}})$ of the effective microscale RVEs. Step 2 through step 4 are then repeated for subsequent mechanical loading increments. From this process the effective electrical properties of the microscale RVEs with electrical tunneling effect and inherent piezoresistive effect of the CNT can be obtained as a function of the applied macroscale homogeneous strain, i.e. the load dependent but reversible macroscale effective piezoresistive response.

In order to compare with measures more commonly used in experiments, the effective resistivities $\rho_{ij}^{\text{eff}}(d, \varepsilon_{kl}^{\text{C}})$ obtained in the transverse plane-strain uniaxial tension and axial tension tests can be converted into their representative nanocomposite gauge factors. For the transverse plane-strain uniaxial tension test, the nanocomposite gauge factor can be obtained as (Ren and Seidel, 2013a)

$$G_{22}^{\text{eff}} = \frac{\frac{\Delta R^{\text{eff}}(\varepsilon_0)}{R^{\text{eff}}(0)}}{\varepsilon_0} = \frac{1}{\varepsilon_0} \left(\frac{\rho_{22}^{\text{eff}}(\varepsilon_0)}{\rho_{22}^{\text{eff}}(0)} \frac{1+\varepsilon_0}{1-\frac{(\nu_{21}^{\text{eff}}+\nu_{31}^{\text{eff}}\nu_{23}^{\text{eff}})\varepsilon_0}{1-\nu_{32}^{\text{eff}}\nu_{23}^{\text{eff}}} - 1 \right)$$
(3.15)

For the axial tension test, the corresponding gauge factor is

$$\mathbf{G}_{z}^{\text{eff}} = \frac{1}{\varepsilon_{0}} \left(\frac{\rho_{33}^{\text{eff}}(\varepsilon_{0})}{\rho_{33}^{\text{eff}}(0)} \frac{1 + \varepsilon_{0}}{(1 - \nu_{31}^{\text{eff}}\varepsilon_{0})^{2}} - 1 \right)$$
(3.16)

¹See verification of the modeling work in Appendix D.

It is worth noticing that for the metal alloy wires commonly used in strain gauges, the initial and final resistivities are the same, so that the gauge factor is governed by the isotropic Poisson's ratio in the transverse plain-strain uniaxial tension test, and results in an approximately linear relationship between normalized change in resistance and strain (i.e. with G as the slope of the curve) for small strains. Similarly, for the axial gauge factor with equal initial and final resistivities, Eqn. (6.6) leads to a ν_{31}^{eff} dependence. For the nanocomposites discussed herein, the initial and final resistivities are not equal, and depend on the parameters associated with electrical tunneling (d, λ) and inherent CNT piezoresistivity ($\mathbf{g}_{ijkl}^{\text{C}}$). Here we discuss the relative influence of both mechanism and of their combined effects on the macroscale effective gauge factors.

3.3 Results and Discussion

For the single-walled CNTs considered herein, the outer radius is chosen to be 0.85nm, with the thickness of the annular region chosen to be 0.34nm (Schadler et al., 1998). The CNT annulus and matrix are taken to be isotropic linear elastic with Young's modulus and Poisson's ratios of 1100 GPa and 0.14 and 2.46 GPa and 0.3, respectively (Saito et al., 1998; Zhou et al., 2008). The initial isotropic resistivity within the CNT annulus is chosen to be $10^{-5} \ \Omega \cdot m$ (Ebbesen et al., 1996; Seidel and Lagoudas, 2009), and the polymer matrix is chosen to be Epoxy which is likewise isotropic with resistivity of $10^{14} \ \Omega \cdot m$ in the absence of electrical tunneling which is within the typical range of values commonly reported for insulating polymers in experiments. Barrier heights for Epoxy have been reported to be on the order of $\lambda = 0.5 - 2.5$ eV (Hu et al., 2012), the range of which will be considered here parametrically. Finally, the inherent piezoresistive gauge factor of 2900 reported in Ref. (Stampfer et al., 2006) will be converted into diagonal isotropic piezoresistive coefficients g_{ijkl}^{C} as discussed in Ref. (Ren and Seidel, 2013a) and applied herein.

3.3.1 Plane-strain uniaxial tension test on the well-dispersed transverse hexagonal RVE

The plane-strain uniaxial tension test as identified in Table 3.1 is applied to the transverse hexagonal RVEs to obtain the effective transverse piezoresistive properties, $\rho_{22}^{\text{eff}}(\tilde{\varepsilon}_0)$ and G_2^{eff} , for strains up to 1%. The influence of the electrical tunneling barrier height is studied over a range of volume fractions up to 60% vol, both independently and in conjunction with inherent CNT piezoresistivity.² The inclusion of both mechanisms leads to evolution in electrical microstructure associated with increasing tensile strain on the RVE as shown in Fig. 3.6.

As seen in Fig. 3.6(a) and Fig. 3.6(b), for the RVEs corresponding to 10%vol and 60%vol CNTs, at zero boundary strain, the shortest CNT-CNT distance are 3.15 nm and 0.39 nm respectively, which are within the cut-off distances of Epoxy at $\lambda = 0.5$ eV. Therefore the electrical tunneling effect takes place, i.e. the volume fractions are above the percolation volume fraction, and the resistivities are significantly reduced in the polymer matrix. While no portion of the matrix retains the original matrix resistivity at these volume fractions, the most direct paths between neighboring CNTs have much lower resistivities, and therefore form clearly visible tunneling paths. Upon application of strain $\varepsilon_0 = 1.0\%$, the 'tunnels' in X₂ direction are observed to be thinner as compared to the ones at $\varepsilon_0 = 0.0\%$ due to the RVEs being stretched in X₂ direction and the resistivities of the CNTs are also changed with the applied boundary strain due to the inherent piezoresistive effect. The change can be more easily observed in the 60%vol RVE, as there is greater strain transfer to the CNTs at higher volume fractions.

²While global volume fractions of 10% vol and higher are considered quite large by experimental standards due to processing issues associated with viscosity increases and dispersion of CNTs within the liquid polymer, such volume fractions are considered here as 1) they more capably demonstrate the combined effects of electrical tunneling and inherent CNT piezoresistivity and 2) they are reflective of locally high volume fractions within CNT bundles.



Figure 3.6: Distribution of the resistivity component ρ_{22} in the transverse hexagonal RVEs under plane-strain uniaxial tension test, in which $\lambda = 0.5$ eV, and $G_c = 2900$. Note that the scale bars are different for the two sets of contours. a) Distribution of ρ_{22} in the 10%vol RVE with the applied boundary strain at $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 1.0\%$. b) Distribution of ρ_{22} in the 60%vol RVE with the applied boundary strain at $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 1.0\%$.

The corresponding effective relative change in resistance, i.e. $\Delta R^{\text{eff}}/R^{\text{eff}}$, as a function of the applied boundary strain for these two volume fractions are provided in Fig. 3.7 for both electrical tunneling and combined tunneling and inherent CNT piezoresistivity cases. For the 10%vol well-dispersed transverse RVE (Fig. 3.7(a)), five cases are considered: 1) only inherent CNT piezoresistivity of $G_c = 2900, 2$) only inherent CNT piezoresistivity of $G_c = 10^{23}, 3$) only electrical tunneling with $\lambda = 1.4 \text{ eV}, 4$) both electrical tunneling $\lambda =$ 1.4 eV and inherent CNT piezoresistivity $G_c = 2900$, and 5) both electrical tunneling $\lambda =$ 1.4 eV and inherent CNT piezoresistivity $G_c = 10^{23}$. As observed in Ref. (Ren and Seidel, 2013a), including only the inherent CNT piezoresistivity mechanism does not lead to large gauge factors in the transverse direction. In fact, for the inherent CNT piezoresistivity is negligible as $\rho_{22}^{\text{eff}}(\varepsilon_0) \approx \rho_{22}^{\text{eff}}(0)$ so that the effective gauge factor is simply that of the







Figure 3.7: The relative change of effective resistance of the microscale RVE with the change of boundary strain ε_0 under plane-strain uniaxial tension test. a) $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the microscale RVE as $\varepsilon_0 = 0.0\% - 1.0\%$, in which there are 10%vol CNTs. b) $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the microscale RVE as $\varepsilon_0 = 0.0\% - 1.0\%$, in which there are 60%vol CNTs.

nominal geometric effect, 1.42. Even with a very large hypothetical CNT gauge factor of $G_c = 10^{23}$, the effective transverse gauge factor of the nanocomposite only increases by 73% to $G_2^{\text{eff}} = 2.45$ at 10%vol. However, if contrast the electrical tunneling effect is independently considered, for a mid range value of Epoxy barrier height of $\lambda = 1.4$ eV, a large relative change of effective resistance of the microscale RVE is observed, an order of magnitude larger at ε_0 than when inherent CNT piezoresistivity is independently considered, yielding a gauge factor of 21.2 at 10%vol. This is because with the applied boundary strain increased from 0%-1%, the CNT-CNT distances are all within the critical tunneling distance of 3.53 nm at $\lambda = 1.4$ eV. Therefore the electrical tunneling effect takes place in the polymer matrix, which is very sensitive to the change of relative locations of the CNT and induces large changes in resistance even with the small boundary strains strains of up to only 1% are applied.

For the cases in which the coupled effect of the electrical tunneling at $\lambda = 1.4$ eV and the inherent piezoresistivity of the CNT are considered, at 10%vol CNT negligible differences in the relative resistance changes are observed between the coupled cases and the independent electrical tunneling results. Even when the large hypothetical $G_c = 10^{23}$ is coupled with electrical tunneling effect, the transverse effective gauge factor at 10%vol only increases by seven tenths to 21.9 at $\varepsilon_0 = 1\%$. This is because in order for the CNT to influence the overall piezoresistive response, the change of resistivity of the CNT has to be comparable to electrical tunneling induced resistivity and resistivity changes within the matrix which at 10%vol CNTs is driving the overall nanocomposite effective transverse resistivity. For example, as seen in Table 3.3, with $G_c = 2900$ the volume averaged resistivity of the CNT is increased from $1.00 \times 10^{-5} \Omega \cdot m$ to $1.17 \times 10^{-5} \Omega \cdot m$ which is period be compared to the effective resistivity.

 $1.00 \times 10^{-5}\Omega \cdot m$ to $1.17 \times 10^{-5}\Omega \cdot m$, which is negligible compared to the effective resistivity of the RVE, which is on the order of $10^{13}\Omega \cdot m$. When the inherent piezoresistivity of the CNT is increased to 10^{23} , the average resistivity of the CNT increases from $1.00 \times 10^{-5}\Omega \cdot m$ to $6.13 \times 10^{13}\Omega \cdot m$, leading to a very modest increase in the nanocomposite transverse effective resistivity of three hundredths over the effective resistivity of the nanocomposite when only electrical tunneling is considered. Thus, at 10% vol CNT and barrier height of $\lambda = 1.4$ eV, the transverse piezoresistive response of the nanocomposite is governed entirely by the electrical tunneling mechanism.

In order to see a larger influence of the inherent piezoresistivity of the CNT on the overall piezoresistive response, one can either increase the volume fraction of the CNT or decrease the height of barrier of the polymer matrix. Through increasing the volume fraction of the CNT, the CNT-CNT distance is decreased, resulting in a lower overall resistivity of the nanocomposites at zero strain (assuming already percolated), and depending on the barrier height can be in a region of the ρ_{tunnel} vs d response which is very sensitive to small changes in d with applied strain. While these observations would seem to make the electrical tunneling effect even more influential than inherent CNT piezoresistivity effect, in actuality, they bring the matrix resistivity to a value closer to that of the CNT such that changes in CNT resistivity (especially with the higher CNT volume fraction) become increasingly significant

Table 3.3: The volume averaged resistivity component $\rho_{\text{CNT}(22)}^{\text{avg}}$ of the CNT and the effective resistivity component $\rho_{\text{RVE}(22)}^{\text{eff}}$ of the 10%vol transverse hexagonal microscale RVE at the applied boundary strains of $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 1.0\%$ respectively of the plane-strain uniaxial tension test.

$\varepsilon_0=0.0\%$	$\rho^{\rm avg}_{\rm CNT(22)}(\Omega\cdot{\rm m})$	$\rho^{\rm eff}_{\rm RVE(22)}(\Omega\cdot{\rm m})$
10% vol & $\lambda = 1.4~{\rm eV}$	1.00×10^{-5}	4.80×10^{13}
10% vol & $\lambda = 1.4 \ \mathrm{eV}$ & $\mathrm{G_c} = 2900$	1.00×10^{-5}	4.80×10^{13}
10% vol & λ = 1.4 eV & $\rm G_c = 10^{23}$	1.00×10^{-5}	4.80×10^{13}
$\varepsilon_0 = 1.0\%$	$\rho_{\rm CNT(22)}^{\rm avg}(\Omega \cdot {\rm m})$	$\rho^{\rm eff}_{\rm RVE(22)}(\Omega\cdot{\rm m})$
10% vol & $\lambda = 1.4~{\rm eV}$	1.00×10^{-5}	5.74×10^{13}
10% vol & $\lambda = 1.4 \ \mathrm{eV}$ & $\mathrm{G_c} = 2900$	1.17×10^{-5}	5.74×10^{13}
10% vol & $\lambda = 1.4~{\rm eV}$ & ${\rm G_c} = 10^{23}$	6.13×10^{13}	5.77×10^{13}

*The volume averaged resistivity component $\rho_{CNT(22)}^{avg}$ corresponds to the CNT annulus and does not include the hollow region of the CNT.

to the overall effective nanocomposite response. In addition, the strains transferred to the CNTs are higher at larger volume fractions, which can induce larger inherent piezoresistive effects of the CNT. As an alternative to increasing the volume fraction, in decreasing the height of the tunneling barrier of the polymer matrix, the electrical tunneling resistivities in the polymer matrix are again decreased, which can also result in a lowered overall resistivity that is more sensitive to the inherent piezoresistivity of the CNT. As seen in Table 3.4, when the volume fraction of the CNT is increased to 60%, the difference between the resistivity of the CNT and effective resistivity of the microscale RVE is reduced to within 1 to 2 orders of magnitude for barrier heights of $\lambda = 0.5$ eV and $\lambda = 1.4$ eV, respectively. As such, the inherent piezoresistivity of the CNT can more effectively influence the overall piezoresistivity of the microscale RVE. The influence of increasing the volume fraction and lowering the barrier height on the relative change in effective resistance can be seen in Fig. 3.7(b). For

the microscale RVE with 60%vol CNT, although the electrical tunneling effect is still the main driving force, the inherent piezoresistivity of the CNT with $G_c = 2900$ is observed to be a contributing factor to the overall piezoresistive response. For the case of $\lambda = 1.4$ eV, the effective gauge factor of the microscale RVE is increased by 0.41 at $\varepsilon_0 = 1.0\%$, and for the case of $\lambda = 0.5$ eV, the effective gauge factor of the microscale RVE is increased by 1.8 relative to the independent electrical tunneling gauge factors at 60%vol CNT.

Table 3.4: The volume averaged resistivity component $\rho_{\text{CNT}(22)}^{\text{avg}}$ of the CNT and the effective resistivity component $\rho_{\text{RVE}(22)}^{\text{eff}}$ of the 60% vol transverse hexagonal microscale RVE at the applied boundary strains of $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 1.0\%$ respectively of the plane-strain uniaxial tension test.

$arepsilon_0=0.0\%$	$\rho_{\rm CNT(22)}^{\rm avg}(\Omega \cdot {\rm m})$	$\rho^{\rm eff}_{\rm RVE(22)}(\Omega\cdot{\rm m})$
60% vol & $\lambda = 1.4~{\rm eV}$	1.00×10^{-5}	1.45×10^{-3}
60% vol & $\lambda = 1.4$ eV & $G_c = 2900$	1.00×10^{-5}	1.45×10^{-3}
60% vol & $\lambda=0.5~{\rm eV}$	1.00×10^{-5}	3.15×10^{-4}
60% vol & $\lambda=0.5~{\rm eV}$ & ${\rm G_c}=2900$	1.00×10^{-5}	3.15×10^{-4}
$\varepsilon_0 = 1.0\%$	$\rho^{\rm avg}_{\rm CNT(22)}(\Omega\cdot{\rm m})$	$\rho^{\rm eff}_{\rm RVE(22)}(\Omega\cdot{\rm m})$
$\varepsilon_0 = 1.0\%$ 60% vol & $\lambda = 1.4~{\rm eV}$	$\begin{aligned} \rho^{\mathrm{avg}}_{\mathrm{CNT}(22)}(\Omega\cdot\mathbf{m}) \\ 1.00\times10^{-5} \end{aligned}$	$\begin{split} \rho^{\rm eff}_{\rm RVE(22)}(\Omega\cdot{\rm m}) \\ 1.69\times10^{-3} \end{split}$
$\varepsilon_0 = 1.0\%$ 60%vol & $\lambda = 1.4 \text{ eV}$ 60%vol & $\lambda = 1.4 \text{ eV}$ & $G_c = 2900$	$\begin{aligned} \rho^{\rm avg}_{\rm CNT(22)}(\Omega \cdot {\rm m}) \\ 1.00 \times 10^{-5} \\ 1.43 \times 10^{-5} \end{aligned}$	$\begin{aligned} \rho^{\rm eff}_{\rm RVE(22)}(\Omega \cdot {\rm m}) \\ 1.69 \times 10^{-3} \\ 1.70 \times 10^{-3} \end{aligned}$
$\varepsilon_0 = 1.0\%$ $60\% \text{vol } \& \ \lambda = 1.4 \text{ eV}$ $60\% \text{vol } \& \ \lambda = 1.4 \text{ eV} \& \text{ G}_c = 2900$ $60\% \text{vol } \& \ \lambda = 0.5 \text{ eV}$	$\begin{aligned} \rho^{\rm avg}_{\rm CNT(22)}(\Omega\cdot{\rm m}) \\ 1.00\times10^{-5} \\ 1.43\times10^{-5} \\ 1.00\times10^{-5} \end{aligned}$	$\rho_{\rm RVE(22)}^{\rm eff}(\Omega \cdot m)$ 1.69×10^{-3} 1.70×10^{-3} 3.43×10^{-4}

*The volume averaged resistivity component $\rho_{CNT(22)}^{avg}$ corresponds to the CNT annulus and does not include the hollow region of the CNT.

The change of the effective resistivity component ρ_{22}^{eff} and the effective gauge factor G_2^{eff} of the microscale RVE with the change of volume fraction of the CNT are shown in Fig. 3.8. As observed in Fig. 3.9(a), at low volume fractions for a given barrier height (i.e. 0%-4.62%vol
Figure 3.8: The change of effective resistivities and gauge factors of the transverse hexagonal microscale RVEs at $\varepsilon_0 = 1\%$ with the change of volume fraction of the CNT. a) The effective resistivity component ρ_{22}^{eff} at $\varepsilon_0 = 1\%$ vs. the change of volume fraction of the CNT from 1% to 60%. b) The effective gauge factor G_2^{eff} at $\varepsilon_0 = 1\%$ vs. the change of volume fraction of the CNT from 1% to 60%.



at $\lambda = 0.5$ eV, 0%-9.59%vol at $\lambda = 1.4$ eV, and 0%-13.8%vol at $\lambda = 2.5$ eV), the effective transverse resistivity is approximately equal to that of the nominal value of the Epoxy matrix as the distances between neighboring CNTs are greater than the respective d_c so that no electrical tunneling is taking place. Over this range of volume fractions, as observed in Fig. 3.9(b), the effective transverse gauge factors are entirely driven by the geometric effect, yielding an average value of around 1.425. With the increase of volume fraction of the CNT, the CNTs become close enough to engage the electrical tunneling effect, i.e. to form an

electrical tunneling induced percolated network. As observed in Fig. 3.9(a), the percolation volume fraction is manifest in the form of a sudden, order of magnitude change in effective transverse resistivity corresponding to a deviation from the nominal volume fraction response of the nanocomposite in the absence of the tunneling effect. As the volume fraction increases beyond the percolation concentration, the separation distance dependence of the tunneling effect leads to continued orders of magnitude deviation of the effective transverse resistivity from the no tunneling effect behavior. It is noted that the lower barrier height results in a lower volume fraction percolation and more rapid decrease in the resistivity. The percolation effect is likewise visible in Fig. 3.9(b) where the effective transverse gauge factors are observed to experience a sharp increase near the percolation concentration from the geometric value to values of 25.9, 33.9, and 41.0 for barrier heights of λ = 0.5 eV, λ = 1.4 eV, and λ = 2.5 eV, respectively. It is worth noting that the effective gauge factors attain a peak value before gradually decreasing with increasing volume fractions above the percolation concentration, and that these peak values increase with increasing barrier height. These observations can be explained in terms of the trade off between larger percolation volume fractions and where the volume fraction places the zero-strain effective resistivity on the ρ_{tunnel} vs d curve (Fig. 3.3(b)) as shown in Table 3.5. At the start of percolation, though at

(Unit: $\Omega \cdot m$)	λ	$0.5 \ \mathrm{eV}$	1.4 eV	$2.5 \ \mathrm{eV}$
	$\rho_{22}^{\text{eff}}(\varepsilon_0 = 0\%)$	2.79×10^{13}	4.80×10^{13}	1.25×10^{13}
per%vol	$\rho_{22}^{\text{eff}}(\varepsilon_0 = 1\%)$	3.44×10^{13}	5.74×10^{13}	1.73×10^{13}
	$G_2^{\text{eff}}(\varepsilon_0 = 1\%)$	25.3	21.2	40.5
	$\rho_{22}^{\text{eff}}(\varepsilon_0 = 0\%)$	6.42×10^1	5.86×10^5	1.28×10^9
20%vol	$\rho_{22}^{\text{eff}}(\varepsilon_0 = 1\%)$	7.43×10^1	7.53×10^5	1.78×10^9
	$G_2^{\text{eff}}(\varepsilon_0 = 1\%)$	17.4	30.2	41.0

Table 3.5: The effective resistivity component ρ_{22}^{eff} and the effective gauge factor G_2^{eff} at the percolating volume fraction and at 20% vol.

different volume fractions all three barrier heights have nearly the same order of magnitude effective resistivity at 1% strain, but very different zero-strain resistivities associated with the barrier height's d_c and associated rate of resistivity change as demonstrated in Fig. 3.3(b). This rate of change of resistivity for the given barrier height then governs the subsequent reduction in effective gauge factor from the peak value leading to the differences observed at a common volume fraction, e.g. 20%vol in Table 3.5. Having a peak gauge factor near the percolation concentration has likewise been reported in experimental characterization efforts for nanocomposites (Kang et al., 2006b, 2009; Bautista-Quijano et al., 2010; Oliva-Aviles et al., 2011; Ferreira et al., 2012b), and is likely also a consequence of this trade off in the electrical tunneling response.

Finally, recalling from Fig. 7 that the inherent CNT piezoresistivity can have an influence on the effective transverse gauge factor at high volume fractions, the combined mechanism effective gauge factors are provided in Fig. 8b for volume fractions between 40% vol and 60%vol for a CNT gauge factor of $G_c = 2900$. It is found that the largest influence the inherent piezoresistivity happens at 60% vol of CNTs and at the lowest barrier height $\lambda =$ 0.5 eV, where the effective gauge factor increases by 17% from 10.5 to 12.3. The influence of the inherent CNT piezoresistivity decreases with decreasing volume fraction due to reduced strain transfer to the CNT, and decreases with increasing barrier height as the tunneling resistivity becomes much larger than the CNT resistivity. For example, at 40% vol of the CNT and barrier height of $\lambda = 0.5$ eV, the effective gauge factor is only increased by 0.03 with the inclusion of inherent CNT piezoresistivity, while at 60% vol the gauge factors are increased by 0.41 and 0.10 for $\lambda = 1.4$ eV and $\lambda = 2.5$ eV, respectively. Therefore we can conclude that in the transverse directions, the influence of inherent piezoresistivity of the CNT on the overall piezoresistive response of the nanocomposites is limited, unless 1) it is coupled with the electrical tunneling effect 2) the volume fraction of the CNT is high, e.g. 60% vol 3) the height of barrier of the polymer matrix is low, e.g. 0.5 eV and 4) gauge factors for the CNT are at least of the order of 2900.

The plane-strain uniaxial tension test is applied to the transverse RVEs in order to observe dispersion effects on the nanocomposite effective piezoresistive response. It has been demonstrated that a RVE with 30 cylindrical inclusions is adequate to represent the effective macroscopic mechanical material properties in aligned fiber composites (Gonzalez and Llorca, 2007), therefore in an analogous manner we have constructed RVEs with 30 CNTs at a volume fraction of 10% vol CNT. The locations of the CNTs are randomly generated under the constraint of no overlapping CNTs, and with CNTs on the boundary periodically reflected on opposing sides of the RVE. For demonstration purposes, two different randomly dispersed RVEs are constructed. Figures 3.9(c) and 3.9(d) provide contour plots of local resistivity for the two RVEs at with and without strain for the barrier height of $\lambda = 1.4$ eV. At zero strain one is able to identify a few tunneling paths which span the vertical dimension of the RVE (denoted by dashed lines) are formed. Under the application of a strain of 1%, tunneling paths in the X_2 direction generally increase in resistivity and narrow in width. In RVE 2, very narrow tunneling paths visible at zero strain have been completely disrupted when the strain is applied. In comparison to the well dispersed hexagonal RVE which is expected to yield at most an orthotropic piezoresistive response, the randomly dispersed RVEs will yield an anisotropic piezoresistive response which will be highly sensitive to the specific dispersion of CNTs. In contrast, with a barrier height of $\lambda = 0.5$ eV, the local resistivity contour distribution of the two RVEs appear more like a statistically isotropic material. This is because with $\lambda = 1.4$ eV, the cut-off distance of the electrical tunneling effect is 3.53nm, whereas the cut-off distance is 5.83nm with $\lambda = 0.5$ eV. With a longer cut-off distance, the CNTs are able to form a well-dispersed percolated network at the volume fraction of 10% vol CNTs where the average distance between the CNTs is 2.09 nm and 2.45 nm in RVEs 1 and 2, respectively, and 3.42 nm in well-dispersed hexagonal. While disruptions in conductive paths on applied strain were relatively easy to observe in Fig. 3.9, for the same strain but

lower barrier height of $\lambda = 0.5$ eV in Fig. 3.10 it is much harder to observe the same phenomenon as most of the tunnels are well within the cut-off distance. Careful inspection of Fig. 3.10(a) reveals increases in width and decreases in resistivity (strengthening) of tunnels at points A and B due to Poisson's contraction in X₁ direction, and the weakening of the tunnel at point C where the tunnel is more aligned with the X₂ direction.



Figure 3.9: The contour distribution of isotropic resistivity in the chosen two random transverse RVEs, in both of which the volume fraction of the CNT is 10%. Note that the scale bars are different for the contours. a) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the first random microscale RVE with $\lambda =$ 1.4 eV and for the transverse hexagonal RVE with $\lambda = 1.4$ eV. b) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the second random microscale RVE with $\lambda = 1.4$ eV. The dashed box regions denote areas in which there are stronger electrical tunneling paths due to the nonuniformity of the distribution of the CNTs.

In order to observe how the randomness of the CNTs influence the overall performance of the material, the relative change of resistance with the applied boundary strain of the microscale



Figure 3.10: The contour distribution of isotropic resistivity in the chosen two random transverse RVEs, in both of which the volume fraction of the CNT is 10%. Note that the scale bars are different for the contours. a) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the first random microscale RVE with $\lambda = 0.5$ eV and for the transverse hexagonal RVE with $\lambda = 0.5$ eV. b) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of 0.0% and 1.0% respectively of the first random microscale RVE with $\lambda = 0.5$ eV. b) The contour distribution of resistivity at the applied boundary strain of 0.0% and 1.0% respectively of the second random microscale RVE with $\lambda = 0.5$ eV.

RVEs are obtained, and are compared with the ones based on the 10%vol transverse hexagonal RVE, as seen in Fig. 3.11(a) and Fig. 3.11(b). As would be expected from the clearly visible changes in tunneling paths in Fig. 3.9, for the barrier height of $\lambda = 1.4$ eV there are large differences in the effective relative resistance, with RVE 1 having an effective relative resistance which is more than double that of the well-dispersed hexagonal RVE at 1% strain while RVE 2 yields a value half that of the hexagonal RVE at the same strain. Such large differences in piezoresistive behavior can be attributed not only to the large barrier height, which dictates sensitivity to changes in the tunneling distance (Fig. 3.3(b)), but also to the number of RVE-spanning tunneling paths and the average tunneling distance between the

Table 3.6: The effective resistivity component ρ_{22}^{eff} , the average distance d^{avg} of the CNTs in the stronger tunneling path, and the average tunneling resistivity $\rho_{\text{tunnel}}^{\text{avg}}$ in the stronger tunneling path of the three transverse microscale RVEs at the barrier heights of $\lambda = 1.4$ eV and $\lambda = 0.5$ eV respectively. Note that the units in the table are $\Omega \cdot m$ for resistivities and nm for lengths.

λ =1.4 eV	RVE 1	Hexagonal RVE	RVE 2
$\rho_{22}^{\rm eff}(\varepsilon_0=0\%)$	2.48×10^{10}	4.80×10^{13}	2.14×10^{13}
$\rho_{22}^{\text{eff}}(\varepsilon_0 = 1\%)$	3.68×10^{10}	5.74×10^{13}	2.30×10^{13}
$d^{\rm avg}(\varepsilon_0 = 0\%)$	2.09	3.42	2.45
$d^{\rm avg}(\varepsilon_0 = 1\%)$	2.11	3.47	2.49
$\rho_{\rm tunnel}^{\rm avg}(\varepsilon_0=0\%)$	2.60×10^6	2.70×10^{13}	2.13×10^8
$\rho_{\rm tunnel}^{\rm avg}(\varepsilon_0 = 1\%)$	3.53×10^6	5.03×10^{13}	3.54×10^8
$\lambda = 0.5 \text{ eV}$	RVE 1	Hexagonal RVE	RVE 2
$\rho_{22}^{\rm eff}(\varepsilon_0=0\%)$	4.51×10^4	5.01×10^6	3.63×10^6
$\rho_{22}^{\text{eff}}(\varepsilon_0 = 1\%)$	5.58×10^4	6.11×10^6	4.38×10^6
$d^{\rm avg}(\varepsilon_0 = 0\%)$	2.09	3.42	2.45
$d^{\rm avg}(\varepsilon_0 = 1\%)$	2.11	3.47	2.49
$\rho_{\rm tunnel}^{\rm avg}(\varepsilon_0=0\%)$	1.65×10^{2}	2.57×10^6	2.30×10^{3}
$\rho_{\rm tunnel}^{\rm avg}(\varepsilon_0 = 1\%)$	1.98×10^{2}	3.73×10^{6}	3.11×10^{3}

CNTs forming the paths. For example, for the unstrained RVE 1, the principal X₂ direction tunneling path (within the dashed line of Fig. 3.9(c)) has an average CNT separation distance of 2.08nm, which is significantly shorter than the separation distance of 3.41nm in the analogous path of the well-dispersed hexagonal RVE. From these values, the average resistivity of the tunneling paths can be estimated as $2.6 \times 10^6 \Omega \cdot m$ in the RVE 1 path which is seven orders of magnitude lower than the value of $2.7 \times 10^{13} \Omega \cdot m$ established in

the hexagonal RVE. As RVE-spanning conductive paths can be expected to follow a rule of mixtures approach towards estimating effective resistivity, it is not surprising that the single low resistivity tunneling path of RVE 1 leads to a zero-strain effective transverse resistivity of $2.48 \times 10^{10} \Omega \cdot m$ which is two orders of magnitude lower than the effective resistivity of the hexagonal RVE under the influence of its greater number of high resistivity tunneling paths. From a similar analysis of the data provided in Table 3.6, one can likewise explain the lower effective relative resistivity of RVE 2 as compared to the hexagonal RVE in Fig. 3.11(a), as well as the much closer behavior of all three RVEs when the barrier height is reduced to λ = 0.5eV as shown in Fig. 3.11(b). These results exemplify the importance of understanding and possibly controlling the microstructural dispersion of CNTs when seeking to obtain ideal nanocomposite gauge factors for specific sensing applications, and can perhaps explain wide range of gauge factors observed from experiments reported in the literature.

3.3.3 Axial tension test on the axisymmetric RVE

In addition to the plane-strain uniaxial tension tests applied to the transverse RVEs, axial tension tests are applied to the axisymmetric RVEs to obtain the effective axial piezoresistive properties. The axial axisymmetric RVEs are chosen to match those used in Ref. (Ren and Seidel, 2013a), and are constructed in such a way that the gap between the tip of the CNT and the top and bottom boundaries of the RVE is only related to the aspect ratio of the CNT, and therefore does not change with the volume fraction of the CNT. Instead, as the aspect ratio of the CNT approaches infinity, the gap approaches zero, and the lateral width approaches that of the transverse hexagonal RVEs so that the finite aspect ratio RVE is consistent with the axial and transverse infinite aspect ratio RVEs. For CNTs with a finite aspect ratio of 300 as chosen here, the tip to tip distance in the axial direction is 0.567 nm, which is within the critical tunneling distance for barrier height of $\lambda = 1.4$ eV, therefore electrical tunneling path is formed in the axial direction. As shown in Fig. 3.12, in both the 1%vol and 20%vol CNT RVEs with finite CNT aspect ratio of 300, at zero strains there is electrical tunneling





Figure 3.11: Comparison of the relative change of effective resistance of the hexagonal microscale RVE and the random microscale RVEs with the change of boundary strain ε_0 under plane-strain uniaxial tension test. a) Comparison of $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the hexagonal microscale RVE and the random microscale RVEs as $\varepsilon_0 = 0.0\% - 1.0\%$, in all of which there are 10%vol CNTs and $\lambda = 1.4$ eV. b) Comparison of $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the hexagonal microscale RVE and the random microscale RVEs as $\varepsilon_0 = 0.0\% - 1.0\%$, in all of which there are 10%vol CNTs and $\lambda = 1.4$ eV. b) Comparison of $\frac{\Delta R^{\text{eff}}}{R^{\text{eff}}}$ of the hexagonal microscale RVE and the random microscale RVEs as $\varepsilon_0 = 0.0\% - 1.0\%$, in all of which there are 10%vol CNTs and $\lambda = 0.5$ eV.

to the ghost CNTs in the RVEs above and below the RVE. The tunneling tip to tip is on the order of $10^{-2}\Omega \cdot m$. In the lateral (transverse) direction of the 1%vol RVE, the CNTs are separated by a distance greater than the critical tunneling distance, and therefore there is no lateral electrical tunneling effect, i.e. the resistivity remains at $10^{14}\Omega \cdot m$ which is the value of the polymer matrix. In the 20% RVE, however, the CNTs are close enough in the lateral directions to have lateral electrical tunneling effects such that the resistivity is decreased from the nominal matrix value to a tunneling value of $10^6\Omega \cdot m$ in the lateral directions. With the application of an axial boundary strain of 0.1%, the separation between the CNT and the ghost CNTs in the axial direction increases, increasing the tunneling resistance at

the tip. In contrast, the tunneling resistivity in the lateral directions decreases as CNTs come closer together in the lateral direction due to Poisson's contraction. As can also be observed in Fig. 3.12, with the inherent piezoresistivity of the CNT turned on, the resistivity of the CNT significantly increases due to the large amount of strain transfer to the CNTs on application of applied boundary strain within the axial RVEs.



Figure 3.12: Distribution of the resistivity component ρ_{zz} in the axisymmetric RVEs under axial tension test, in which the aspect ratio of the CNT is 300, $\lambda = 1.4$ eV, and G_c = 2900 (G_c is converted to $g_{zz} = 2.84 \times 10^2 \Omega \cdot m$ as inputs for our model (Ren and Seidel, 2013a)). Note that the scale bars are different for the two sets of contours. a) Distribution of ρ_{zz} in the 1%vol RVE with the boundary strain applied at $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 0.1\%$. b) Distribution of ρ_{zz} in the 20%vol RVE with the boundary strain applied at $\varepsilon_0 = 0.0\%$ and $\varepsilon_0 = 0.1\%$.

The influence of both barrier height and volume fraction on the piezoresistive response of the axial RVE under uniaxial tensile loads is provided in Figs 3.13 and 3.14. It has been shown in (Ren and Seidel, 2013a) that the inherent piezoresistivity of the CNT itself can not drive the overall piezoresistive response of the nanocomposites in the axial direction, therefore the focus is on the axial electrical tunneling effect and the coupled effect of electrical tunneling



Figure 3.13: The relative change of effective resistance of the 5% vol and 20% vol axisymmetric microscale RVEs with the change of boundary strain ε_0 from 0%-0.1% under axial tension test. The top two curves consider both of the electrical tunneling effect at $\lambda = 1.4$ eV and the inherent piezoresistivity of the CNT with $G_c = 2900$. The bottom two curves consider only the electrical tunneling effect at $\lambda = 1.4$ eV.

and the inherent piezoresistivity of the CNT.

As observed in Fig. 3.13, for both of the 5% vol and the 20% vol axisymmetric RVEs, with the electrical tunneling effect at $\lambda = 1.4$ eV, large piezoresistive response can be observed. At the volume fraction of 1%, the effective axial gauge factor is $G_z^{\text{eff}} = 530$ at $\varepsilon_0 = 0.1\%$, and at the volume fraction of 20%, the effective gauge factor is 1105 at $\varepsilon_0 = 0.1\%$. By coupling the inherent piezoresistivity of the CNT with the electrical tunneling effect, the combined piezoresistive response of the axial microscale RVE is much larger than was observed in the transverse RVEs. For example, at the volume fraction of 1%, the effective gauge factor is increased from 530 to 1033 at $\varepsilon_0 = 0.1\%$ when a CNT gauge factor of $G_c = 2900$ is applied. Similarly, at a volume fraction of 20% vol, the gauge factor is increased from 1105 to 1575. The observed large piezoresistive responses in the axisymmetric RVEs demonstrate that as long as there is electrical tunneling path in the axial direction, the overall piezoresistive response is sensitive to not only the electrical tunneling effect, but also to the inherent piezoresistivity of the CNT.

The effective piezoresistive response under independent electrical tunneling and combined

tunneling and inherent CNT piezoresistivity is provided in Fig. 3.14 for a range of volume fractions up to 60%vol CNT and strains up to 0.1%. As observed in Fig. 3.14(a), at zero strain, when the volume fraction of the CNT increases from 5% vol to 60%, the effective axial resistivity decreases from $1.58 \times 10^{-3} \Omega \cdot m$ to $1.28 \times 10^{-4} \Omega \cdot m$, a much smaller change with volume fraction than was observed in Fig. 3.9(a) for the post percolation behavior of the transverse hexagonal RVE of ten orders of magnitude. Also unlike Fig. 3.9(a), there is no identifiable percolation concentration. This is due to the fixed finite aspect ratio gap size at all volume fractions in the axial RVEs, and because the aforementioned gap size is within the tunneling distance, and therefore is percolated in the axial direction by the same amount at all volume fractions. Further, as noted, the axial tunneling resistivity is orders of magnitude larger than the lateral tunneling resistivity at all volume fractions considered such that the lateral percolation is dwarfed by the axial tunneling. As such, the axial RVEs can be viewed as following the rule of mixtures for effective axial resistivity of the nanocomposite based on an effective wire model consisting of the CNT and the tunneling resistivities at the tips. On application of even very small strains, the effective axial piezoresistive response is governed by the tip to tip tunneling and, when the inherent CNT piezoresistivity is considered, the excellent axial strain transfer of the axial RVEs. The result is very large effective axial gauge factors which, as observed in Fig 13b, also do not demonstrate a noticeable impact of the lateral percolation of the axial RVE. It can therefore be deduced that the axial piezoresistive response as modeled herein will be strongly sensitive to the barrier height and to the aspect ratio of the CNT.

3.4 Conclusions

The macroscale piezoresistive response of carbon nanotube (CNT)-polymer nanocomposites has been explored in terms of a combination of the nanoscale mechanisms of electrical tunneling and CNT inherent piezoresistivity within a computational micromechanics finite element approach using both axial and transverse RVEs for aligned randomly and well-dispersed CNT



Figure 3.14: The change of effective resistivities and gauge factors of the axisymmetric microscale RVEs with the change of volume fraction of the CNT and the applied boundary strain ε_0 . The electrical tunneling effect is considered at $\lambda = 1.4$ eV. a) The change of effective resistivity component ρ_{zz}^{eff} of the microscale RVE with the change of volume fraction of the CNT from 5% to 60% and with the change of applied boundary strain from 0.0% to 0.1%. b) The change of effective gauge factor G_z^{eff} of the microscale RVE with the change of volume fraction of the CNT from 1% to 60%, when the applied boundary strain is at 0.1%.

distributions over a range of volume fractions.

It is found that in the transverse directions: 1) The electrical tunneling effect is the main driving force for the overall piezoresistive response of the nanocomposites. 2) The influence of inherent piezoresistivity of the CNT on the overall piezoresistive response of the nanocomposites is limited, unless a) it is coupled with the electrical tunneling effect b) the volume fraction of the CNT is very high, e.g. 60%vol c) the height of the tunneling barrier of the polymer matrix is low, e.g. 0.5 eV and d) CNT gauge factors of 2900 or higher are used. 3)

There is a percolation concentration where both zero-strain effective transverse resistivity and gauge factors demonstrate large sudden shifts in behavior, and that this percolation concentration is tied to the barrier height such that lower barrier height leads to lower volume fraction percolation. 4) A peak gauge factor near the percolation concentration is observed as is commonly reported in experimental observations in the literature.

It is found that in the axial directions: 1) The tip to tip electrical tunneling effect is the main driving force for the axial piezoresistive response of the nanocomposites. 2) Due to good strain transfer in the axial RVEs, the inherent piezoresistivity of the CNT is an important contributing factor to the axial piezoresistive response. 2) The axial piezoresistive response can be orders of magnitude larger than the transverse response, and can be very sensitive to changes in CNT aspect ratio.

Finally, it is noted that the current modeling efforts yield percolation volume fractions and gauge factors which are larger than are typically observed in experiments (i.e. percolation concentrations of 0.074% wt of the CNT (Kim et al., 2003) and gauge factors on average of 4-5). This is largely because of the assumption of well-aligned CNTs within the matrix and the subsequent use of simplified 2D RVEs. Given the strong sensitivities observed between the well-dispersed and randomly dispersed transverse RVEs, one can anticipate that the full 3D dispersion and misorientation of CNTs within as produced nanocomposite samples tested in laboratory experiments will have a tremendous impact on the observed piezoresistive response, leading to a combination of some of the aspects observed from both the axial and transverse cases studied herein, e.g. a lower volume fraction percolation associated with even slight misorientation and slightly less than perfect distribution (to establish fewer but stronger conducting percolated paths than in well-dispersed cases). Thus, it is believed that the results provided herein have some practical application towards understanding and tailoring nanocomposite piezoresistive strain sensor design, for example, as in fuzzy fiber strain sensors (Yamamoto et al., 2009, 2012; Chatzigeorgiou et al., 2012; Ren and Seidel, 2011) which can take advantage of both the axial and transverse piezoresistive responses from the radially oriented CNT network nanocomposite surrounding a glass fiber, e.g. having Xiang Ren

$Chapter \ 3$

high gauge factor CNT alignment direction in the direction of expected smallest strain and percolated concentration of CNTs in the transverse direction of highest strain.

Modeling of Dispersion Effect on the Piezoresistivity of Carbon Nanotube-Polymer Nanocomposites via 3D Computational Multiscale Micromechanics Methods

4.1 Introduction

It has been found in the literature that the gauge factor of the nanocomposites, which is used to measure the strength of mechanical-electrostatic coupling within the material, can vary in a relatively large range, as seen in Fig. 4.1. The maximum gauge factors are achieved at a concentration just above or a few times larger than the percolation threshold concentration (Kang et al., 2006b, 2009; Bautista-Quijano et al., 2010; Oliva-Aviles et al., 2011; Ferreira et al., 2012b; Ku-Herrera et al., 2013), which makes CNT polymer nanocomposites very attractive in the manufacturing of high gauge-factor light-weight strain gauges (Watkins et al., 2004; Loh et al., 2005; Veedu et al., 2006; Kang et al., 2006a,b; Zhang et al., 2006; Boger et al., 2008; Kang et al., 2009; Wichmann et al., 2009; Song et al., 2009; Gao et al., 2009a; Thostenson et al., 2009; Yamamoto et al., 2012).



Figure 4.1: Gauge factors of the CNT polymer nanocomposites under tension and compression as found in the literature (Kang et al., 2006b; Zhang et al., 2006; Wichmann et al., 2009; Kang et al., 2009; Bautista-Quijano et al., 2010; Oliva-Aviles et al., 2011; Ferreira et al., 2012b; Ku-Herrera et al., 2013).

Currently, several nanoscale mechanisms have been identified to contribute to the overall piezoresistive response of the CNT polymer nanocomposites, including the electrical tunneling effect (electron hopping) (Simmons, 1963; Fuhrer et al., 2000; Budlum and Lu, 2001; Li et al., 2007; Xia and Curtin, 2007; Li and Chou, 2008; Li et al., 2008; Theodosiou and Saravanos, 2010; Hu et al., 2012), the inherent piezoresistive effect of the CNT (Rochefort et al., 1999; Peng and Cho, 2000; Tombler et al., 2000; Cao et al., 2003; Dharap et al., 2004; Stampfer et al., 2006; Megalini et al., 2009; Theodosiou and Saravanos, 2010), and the network effect of the CNTs. Due to Van der Waals forces, the CNTs tend to form bundles of large aspect ratios, and depending on the processing techniques, the CNT bundles tend to form networks with specific patterns, e.g. randomly dispersed or aligned. The network of the CNTs not only results in the nanocomposites being electrically percolated at extremely low weight percentages of the CNT, but also plays a key role in determining the overall piezore-

Efforts to model the piezoresistive response of nanocomposites have included resistor network models (Li and Chou, 2008; Theodosiou and Saravanos, 2010; Hu et al., 2012) and micromechanics models (Ren and Seidel, 2013a,b) based on finite element analysis (FEA). The advantage of the resistor network model is that it can capture the randomness of the CNTs in a more direct sense by modeling the CNTs as rectangles or cylinders that are randomly dispersed in the 2D or 3D unit cell. The disadvantage of the model is that it does not precisely obtain the local kinematics and electrostatics of the CNT and the polymer matrix within the network which are crucial for modeling the piezoresistive response of the nanocomposites. On the other hand, although the micromechanics models based on FEA can more precisely obtain the kinematics and electrostatics of the local nanocomposite representative volume elements (RVE), due to computational challenges in terms of meshing and large degrees of freedom, these models have only been focused on the local transverse and axial tip-to-tip piezoresistive responses of the CNT bundles (Ren and Seidel, 2013a,b). Without the 3D network effect, the micromechanics models have not explained why the electrical percolation and the piezoresistive responses of the nanocomposites can occur at such low CNT weight percentages and why the measured gauge factors can vary significantly in experiments.

In this study, to model the piezoresistive response of the macroscale nanocomposite specimen and to tackle the multiscale nature of the problem, a 3D computational multiscale piezoresistive model is developed. In this model, a 3D cubic mesoscale RVE and a 3D hexagonal nanoscale RVE are used respectively to represent the macro and nano scale materials, and the electrical tunneling effect and the inherent piezoresistivity of the CNT are considered within the nanoscale RVE. In order to account for the network effect of the CNTs, the nanoscale RVEs are intentionally dispersed within the mesoscale RVE to study the dispersion and network effects on the overall piezoresistive response of the nanocomposites. The computations for the multiscale model employ a bottom-up/top-down/bottom-up approach, and the discussion of the results are focused on the piezoresistive gauge factor sensitivity to CNT distributions.

4.2 Model Description

4.2.1 Schematics of the 3D computational multiscale model



Figure 4.2: Schematics of the 3D computational multiscale micromechanics model for the nanocomposite specimen under uniaxial tension or compression test. a) The macroscale nanocomposite specimen under uniaxial tension or compression test. b) The mesoscale RVE (1 mm^3) for the nanocomposite material within the specimen. Note that in real computations the number of elements used is 8000, i.e. 64000 subelements. c) One single hexahedron element within the mesoscale RVE. d) Illustration of the CNT bundle within the subelement. e) The nanoscale RVE representing the CNT bundle. Note that $\tilde{}$ on the coordinate system denotes the macroscale whereas the $\hat{}$ denotes the nanoscale, with the mesoscale denoted with an unmodified X_i coordinate system.

The macroscale boundary value problem selected for the present work consists of a nanocomposite dogbone specimen with electrodes for monitoring the macroscale piezoresistive re-

sponse (Fig. 6.5a). As such a configuration corresponds to a uniform state of strain and electric field at the macroscale, a representative cube of nanocomposite material of dimension 1 mm is taken to construct the mesoscale RVE, as seen in Fig. 6.5b. The mesoscale RVE is meshed by eight-node linear hexahedron elements. For each element, there are eight subelements surrounding the eight gaussian integration points, as seen in Fig. 6.5c. Within each subelement, it is assumed that the material is either pure polymer matrix or polymer nanocomposites reinforced by CNT bundles, which can be aligned in any orientation, as seen in Fig. 6.5d. To simplify the problem, it is further assumed that the individual CNTs within the bundle are arranged in a hexagonal packing, locally aligned, and have infinite aspect ratios, for which the hexagonal nanoscale RVE (Hammerand et al., 2007) as shown in Fig. 6.5e is used. Although the CNT orientation and weight (or volume) percentage of the local nanoscale RVE are not necessarily the same for the subelements, the global weight percentage of the CNT in the mesoscale RVE is fixed while different dispersions are considered.

In order to show the possible CNT dispersion scenarios, a diagram of CNT dispersions for the 3D multiscale model is shown in Fig. 4.3. The diagram is constructed based on 1-2-3 coordinates, which are the three dispersion factors considered: 1. the CNT subcell dispersions, 2. the local CNT orientations, and 3. the local CNT volume fraction variations. It can be seen that in +1 direction, the dispersion of the subcells is transited from the extreme of statistically well dispersed, to the intermediate of partially columned, and further to another extreme of fully agglomerated. In +2 direction, the local orientation of the CNTs within the subcell are transited from the extreme of vertically aligned to the intermediate of randomly aligned, and further to another extreme of transversely aligned. In +3 direction, the distribution of local subcell volume fractions of the CNT is transited from the extreme of all equal to each other but not equal to the global volume fraction, and further to another extreme of all equal to each other and also equal to the global volume fraction. The diagram is intended to show a whole spectrum of the CNT dispersion possibilities for the

3D multiscale model. However, it is not wise and impossible to analyze all the dispersion scenarios, as such, we pick up a few of them to discuss the CNT dispersion effects on the overall piezoresistive response of the CNT-polymer nanocomposites, as is to be introduced in section 7.3.



Figure 4.3: The diagram of CNT dispersions for the 3D multiscale model. Note that the subcells correspond to the subelements of the mesoscale RVE. Also note that the scenarios of a) to g) illustrated here are in 1-3 plane.

4.2.2 Computational procedures for the 3D multiscale model

The computations are conducted by using an in-house multiscale finite element code, which are summarized here. By assuming the mechanical properties of the CNT and the polymer matrix to be linear elastic under small strain assumptions, the nanoscale effective stiffness tensor $\hat{\mathbf{C}}^{\text{eff}}$ of the local nanocomposites reinforced by CNT bundles is first obtained from the computational micromechanics method by solving several periodic boundary value problems on the hexagonal nanoscale RVE (Hammerand et al., 2007). The nanoscale effective stiffness is then substituted into the integration points of the mesoscale RVE by coordinate transformation (Ren et al., 2014). By applying the computational micromechanics method again, i.e. solving the same periodic boundary conditions but at the microscale, the effective mechanical stiffness tensor \mathbf{C}^{eff} of the mesoscale RVE is obtained.

Once the mechanical properties of the multiscale model are obtained following the bottom-up algorithm, load increments are applied following a top-down algorithm. The homogeneous macroscale strain field $\tilde{\varepsilon}$ of the specimen is applied to the mesoscale RVE as periodic boundary conditions, under which the mesoscale strain tensor ε at every integration point of the mesoscale RVE is obtained. These mesoscale strains are then applied to the nanoscale RVEs as periodic boundary conditions by coordinate transformation, such that the local kinematics of the nanoscale RVEs at all the locations within the mesoscale RVE can be obtained. The electrical tunneling algorithm within the finite element domain has been discussed in detail in our previous work in (Ren and Seidel, 2013b). Applying this algorithm to all matrix points in the well-dispersed hexagonal nanoscale RVEs leads to clearly visible pattern of tunneling paths within the matrix for percolated weight percentages (Ren and Seidel, 2013b; Ren et al., 2014). The shape and conductivity/resistivity of these tunneling paths are dependent on the relative locations of the CNTs within the hexagonal nanoscale RVE and therefore are evolving in accordance with the local mesoscale strain applied at the boundary of the nanoscale RVE. The second mechanism within the nanoscale RVEs is the inherent piezoresistivity of the CNT, which depends on the strains within the CNT. The CNTs are expected to exhibit

inherent piezoresistivity such that the change in resistivity is related to the strain in the CNT through the piezoresistive strain coefficients as (Ren and Seidel, 2013a)

$$\Delta \hat{\rho}_{ij}^{\rm C} = \hat{\mathbf{g}}_{ijkl}^{\rm C} \hat{\varepsilon}_{kl} \tag{4.1}$$

Here, for simplified demonstration purposes, it is further assumed that $\hat{g}_{1111} = \hat{g}_{2222} = \hat{g}_{3333}$ with all other \hat{g}_{ijkl} being zero.

Once the distribution of resistivities within the nanoscale RVEs is obtained, the effective electrical properties are obtained following again a bottom-up algorithm. The electrical energy equivalence method (Ren and Seidel, 2013a) is used to obtain the effective electrostatic properties $\hat{\rho}_{ij}^{\text{eff}}$ of the nanoscale RVE, which are then substituted into the integration points of the mesoscale RVE by coordinate transformation to represent the effective electrostatic properties of the mesoscale elements. The electrical energy equivalence method is then used again to obtain the effective electrostatic properties ρ_{ij}^{eff} of the nanoscale electric field, are taken to be representative of the macroscale effective properties of the nanocomposite. Therefore under the applied macroscale strain field, correlation between the mechanical and electrostatic properties (i.e. piezoresistivity) of the macroscale nanocomposite specimen can be obtained, with the macroscale effective gauge factor obtained from the equation below (Ren and Seidel, 2013a):

$$G_{33}^{\text{eff}} = \frac{1}{\tilde{\varepsilon}_{33}} \left(\frac{\rho_{33}^{\text{eff}}(\tilde{\varepsilon}_{33})}{\rho_{33}^{\text{eff}}(0)} \frac{1 + \tilde{\varepsilon}_{33}}{(1 - \nu_{31}^{\text{eff}}\tilde{\varepsilon}_{33})(1 - \nu_{32}^{\text{eff}}\tilde{\varepsilon}_{33})} - 1 \right)$$
(4.2)

in which $\rho_{33}^{\text{eff}}(\tilde{\varepsilon}_{33})/\rho_{33}^{\text{eff}}(0)$ is driven from the nanoscale piezoresistive mechanisms of the material, such as the electrical tunneling effect and inherent piezoresistivity of the CNT. If there is only geometric effect, i.e. if the material itself is not piezoresistive, Eq. 6.6 is reduced to

$$G_{33}^{\text{eff}} = \frac{1}{\tilde{\varepsilon}_{33}} \left(\frac{1 + \tilde{\varepsilon}_{33}}{(1 - \nu_{31}^{\text{eff}} \tilde{\varepsilon}_{33})(1 - \nu_{32}^{\text{eff}} \tilde{\varepsilon}_{33})} - 1 \right)$$
(4.3)

4.3 Results and Discussion

The modeling work is focused on the piezoresistive response of macroscale nanocomposite specimen under small uniaxial tension and compression tests (| $\tilde{\varepsilon}$ |< 1.0%). To be consistent with experiments, the study is focused on the MWCNT/Epoxy vinyl ester (VE) nanocomposites with 1.0% wt (CNT weight/VE weight) of the CNT (Ku-Herrera et al., 2013), with the weight percentages converted to volume percentages based on the densities of the CNT and the polymer (the densities of the CNT and VE are 1.4g/cm³ and 1.17g/cm³ respectively). According to (Aviles et al., 2012), the outer and inner diameters of MWCNTs are chosen to be 13 nm and 4 nm respectively. The Young's modulus and Poisson's ratio of the CNT are taken to be 1100 GPa and 0.14 (Saito et al., 1998). The Young's modulus of VE is 3.60 GPa (Ashland Performance Materials), and the Poisson's ratios of VE is chosen to be 0.3. The initial isotropic resistivity within the CNT annulus is chosen to be $10^{-5} \Omega \cdot m$ (Ebbesen et al., 1996; Seidel and Lagoudas, 2009), and VE is likewise isotropic with resistivity of 10^{15} $\Omega \cdot m$ in the absence of electrical tunneling, which is within the typical range of values commonly reported for insulating polymers in experiments. For the electrical tunneling effect within the polymer matrix, an average barrier height of $\lambda = 1.5 \text{ eV}$ (Hu et al., 2012) is considered for VE. In the studies of (Chen and Weng, 2007; Theodosiou and Saravanos, 2010) the reported CNT inherent piezoresistive gauge factors are ≤ 7 under small strains, while in contrast, in (Stampfer et al., 2006) the reported CNT inherent piezoresistive gauge factor can be as large as 2900. In this study a CNT inherent gauge factor of 10 will be converted into diagonal isotropic piezoresistive coefficients \hat{g}_{ijkl}^{C} (Ren and Seidel, 2013a) to study its influence on the overall piezoresistive response of the CNT-polymer nanocomposites.

4.3.1 The first CNT dispersion scenario

This scenario corresponds to scenario g) of the diagram as shown in Fig. 4.3, such that the CNT subcells are statistically well dispersed and for every subcell the CNT local volume



Figure 4.4: The 3D multiscale model for scenario 1. a) Illustration of the mesoscale RVE with well-dispersed, randomly oriented, and 1.0%wt nanoscale RVEs. b) Illustration of the 1.0%wt nanoscale RVE under the transformed mesoscale strain field of $\varepsilon' = R\varepsilon R^{-1}$, in which R can be found in Ref. (Ren et al., 2014) (Displacement magnification factor: 37).

fraction is equal to the global volume fraction of the nanocomposites. As such, the mesoscale and nanoscale RVEs for this scenario are illustrated in Fig. 4.4(a) and Fig. 4.4(b) respectively. For every subelement of the mesoscale RVE, there is a nanoscale RVE to represent the local nanoscale responses. As the local nanoscale weight percentage of the hexagonally packed CNTs equals to the global weight percentage, which is chosen to be 1.0% wt, the CNT separation distances at the nanoscale (110.8 nm) are far greater than the maximum hopping range (Ren and Seidel, 2013b) (3.59 nm) for the hopping barrier considered herein (1.5 eV). As such, only the inherent CNT piezoresistivity mechanism is active in these cases. Following the bottom-up algorithm, the mesoscale RVE's effective mechanical properties are obtained first and summarized in Table 4.1. The mechanical properties of the pure polymer matrix are also listed in Table 4.1 for comparison purposes. It can be seen that in agreement with the CNT dispersion symmetries, the nanocomposites with 'vertical' and 'transverse' CNTs both yield transversely isotropic effective mechanical properties, with the axis of symmetries in X₃ direction. In contrast, the nanocomposites with 'random' CNTs yield isotropic effective mechanical properties. In addition, due to adding of CNTs, the mechanical properties are greatly strengthened, especially in the directions in agreement with the CNT orientations. For example, compared to the pure polymer matrix, the nanocomposites with 'vertical'

CNTs have a 228% increase in the effective Young's modulus of E_{33}^{eff} . The nanocomposites with 'transverse' CNTs have increases of 57% and 71% respectively in the effective in-plane properties of κ_{12}^{eff} and μ_{12}^{eff} . In contrast, for the nanocomposites with randomly oriented CNTs, although the effective Young's modulus is only improved by 36%, in exchange the improvement can be in any spatial direction.

Table 4.1: The effective mechanical properties of the mesoscale RVE for scenario 1 (Unit: GPa). Note that 'vertical' represents that the CNTs align in X_3 direction, 'transverse' represents that the CNTs are randomly dispersed in $X_1 - X_2$ plane, and 'random' represents that the CNTs are randomly dispersed in the 3D space.

Orientation	$\kappa_{12}^{\mathrm{eff}}$	$\mu_{12}^{\rm eff}$	$\mu_{13}^{\rm eff}$	E_{33}^{eff}	ν_{31}^{eff}
Vertical	3.501	1.403	1.408	11.82	0.298
Transverse	5.440	2.371	1.405	4.098	0.192
Orientation	E^{eff}	ν^{eff}			
Random	4.910	0.289			
Pure Polymer	3.600	0.300			

Having solved the mechanical problem by using the bottom-up algorithm, the macroscale strain field ($\tilde{\varepsilon}_{33} = 0\%$ to $\pm 1\%$, $\tilde{\varepsilon}_{11} = -\nu_{31}^{\text{eff}} \tilde{\varepsilon}_{33}$, $\tilde{\varepsilon}_{22} = -\nu_{32}^{\text{eff}} \tilde{\varepsilon}_{33}$) is applied to the cubic mesoscale RVE by using the top-down algorithm through 10 equally increased load steps. As an illustration, the strain distribution of the mesoscale RVE with randomly oriented CNTs and under the macroscale field of ($\tilde{\varepsilon}_{33} = 1\%$, $\tilde{\varepsilon}_{11} = -\nu_{31}^{\text{eff}} \tilde{\varepsilon}_{33}$, $\tilde{\varepsilon}_{22} = -\nu_{32}^{\text{eff}} \tilde{\varepsilon}_{33}$) is shown in Fig. 4.5. The mesoscale strain field at every integration point of the mesoscale RVE is then rotated to the local nanoscale coordinates and applied to the nanoscale RVE, such that the strains in the CNTs and the distances between them are obtained and used to update the electrical resistivities within the nanoscale RVE. The resistivity distribution of the nanoscale RVE at an integration point of the mesoscale RVE and under the macroscale

strain field of ($\tilde{\varepsilon}_{33} = 1\%$, $\tilde{\varepsilon}_{11} = -\nu_{31}^{\text{eff}} \tilde{\varepsilon}_{33}$, $\tilde{\varepsilon}_{22} = -\nu_{32}^{\text{eff}} \tilde{\varepsilon}_{33}$) is shown in Fig. 4.4(b). It can be seen that the change of resistivities is only limited within the CNTs. This is because as mentioned before, for this CNT dispersion scenario the CNTs are far away from each other, therefore the inherent piezoresistivity of the CNT is the only active piezoresistive mechanism. Following the bottom-up algorithm again, the effective resistivities $\hat{\rho}^{\text{eff}}$ of the nanoscale RVE are obtained by using the energy equivalence method, and are rotated back into the mesoscale coordinate system to represent the integration point of the mesoscale RVE, such that $\rho = \hat{\rho}^{\text{eff}}$. As an illustration, the distribution of resistivities of the mesoscale RVE, with randomly oriented CNTs and under the macroscale field of ($\tilde{\varepsilon}_{33} = 1\%$, $\tilde{\varepsilon}_{11} = -\nu_{31}^{\text{eff}} \tilde{\varepsilon}_{33}$, $\tilde{\varepsilon}_{22} = -\nu_{32}^{\text{eff}} \tilde{\varepsilon}_{33}$) is shown in Fig. 4.4(a). Finally, the energy equivalence method is used again to obtain the effective resistivities ρ^{eff} of the mesoscale RVE, which are used to represent the macroscale, such that $\tilde{\rho}^{\text{eff}} = \rho^{\text{eff}}$. Therefore the correlation (piezoresistivity) between the applied macroscale strain field $\tilde{\varepsilon}$ and the macroscale effective resistivities $\tilde{\rho}^{\text{eff}}$ of CNTpolymer nanocomposites is obtained, and the gauge factor can be further obtained following Eqn. 6.6.



Figure 4.5: Strain distribution of the mesoscale RVE under the macroscale strain field of $(\tilde{\varepsilon}_{33} = 1\%, \tilde{\varepsilon}_{11} = -\nu_{31}^{\text{eff}}\tilde{\varepsilon}_{33}, \tilde{\varepsilon}_{22} = -\nu_{32}^{\text{eff}}\tilde{\varepsilon}_{33})$. Within the mesoscale RVE there are hexagonally packed and randomly oriented 1.0% wt CNTs in each subelement.

The relative change of effective resistivity ρ_{33}^{eff} of the mesoscale RVE with the change of macroscale strain $\tilde{\varepsilon}_{33}$ is shown in Fig. 4.6, and the zero-strain effective resistivities $\rho_{33(0)}^{\text{eff}}$ and





Figure 4.6: The relative change of effective resistivity $\Delta \rho_{33}^{\text{eff}} / \rho_{33(0)}^{\text{eff}}$ of the mesoscale RVE when the macroscale strain $\tilde{\varepsilon}_{33}$ is from 0% to ±1%. Note that for every subelement the nanoscale RVE is randomly oriented with the CNT gauge factor of 10.

tensile and compressive effective gauge factors $(G_{33}^{\text{eff}(T)} \text{ and } G_{33}^{\text{eff}(C)})$ of the mesoscale RVE for different CNT orientation cases are summarized in Table 4.2. From Table 4.2 it can be seen that the nanocomposites with 'vertical' CNTs have the lowest zero-strain effective resistivity of $1.33 \times 10^{-3} \ \Omega \cdot m$ and the largest tension/compression gauge factors of 10, and subsequently are the 'random' and 'transverse' nanocomposites. This is because as the nanocomposites with 'vertical' CNTs have all of the CNTs align in X_3 direction, the material is most easily electrically percolated by the CNTs, and the zero-strain effective resistivity satisfies the rule of mixtures by the CNT and the polymer matrix. The inherent piezoresistivity of the CNT is therefore most easily be transferred to the upper scales to induce the strongest macroscale piezoresistive response (Fig. 4.6). To the contrary, as the nanocomposites with 'transverse' CNTs have all of the CNTs disperse in $X_1 - X_2$ plane, the material can not be electrically percolated by the CNTs in X₃ direction, but is rather nearly the same electrically insulating as the pure polymer matrix. In this case the inherent piezoresistivity of the CNT can not be transferred to the upper scales and the tension/compression gauge factors are entirely from the geometric effect. For the nanocomposites with random CNTs, the material is electrically percolated by the random oriented CNTs, and its performances lie between the

two extreme orientation cases. From Fig. 4.6 and Table 4.2 it can also be seen that the relative change of effective resistivity ρ_{33}^{eff} and gauge factors of the mesoscale RVE show good tension/compression symmetries for all the CNT orientation cases. This is because 1) the inherent piezoresistivity of the CNT is linear and symmetric with the applied strains on the CNT (Ren and Seidel, 2013a), 2) under small macroscale tension and compression, the strains on the CNTs within the mesoscale RVE are also linear and symmetric, and 3) under small macroscale strains the mesoscale RVE's geometric effect itself has good tension/compression symmetry. From the results, it can be seen that as long as the material can be electrically percolated by the CNTs themselves, the inherent piezoresistivity of the CNT can have an important influence on the macroscale piezoresistivity of the CNT-polymer nanocomposites.

Table 4.2: The zero-strain resistivities $\rho_{33(0)}^{\text{eff}}$ (Unit: $\Omega \cdot \mathbf{m}$), tensile gauge factors $\mathbf{G}_{33}^{\text{eff}(\mathbf{T})}$, and compressive gauge factors $\mathbf{G}_{33}^{\text{eff}(\mathbf{C})}$ of the mesoscale RVE for scenario 1. Note that the gauge factors are computed at $\tilde{\varepsilon}_{33} = 1\%$.

Orientation	$ ho_{33(0)}^{ m eff}$	$G_{33}^{\mathrm{eff}(\mathrm{T})}$	$G_{33}^{\mathrm{eff}(\mathrm{C})}$
Vertical	1.33×10^{-3}	10	10
Transverse	9.84×10^{14}	1.4	1.4
Random	4.39×10^{-3}	5.4	5.4
Pure Polymer	1.00×10^{15}	1.6	1.6

4.3.2 The second and third CNT dispersion scenarios

In most CNT-polymer nanocomposites as produced in laboratories, due to Van der Waals forces, it is perceivable that the CNTs are more likely to be locally agglomerated instead of well dispersion. To capture the CNT agglomeration effect, the second and third CNT dispersion scenarios are studied, which correspond to scenario e) and d) respectively of the diagram in Fig. 4.3. For the second scenario, the CNT subcells are statistically well dispersed and for every subcell the CNT local weight percentage is much higher than the global weight percentage of the nanocomposites. For the third scenario, the CNT subcells are partially well-dispersed and partially columned, and again for every subcell the CNT local weight percentage is much higher than the global weight percentage. The columns are intended to model the mesoscale conductive paths formed by the CNTs.

The nanoscale RVE for scenario 2 is chosen to have 62.5%vol of the CNT (CNT weight/VE weight = 200%wt), as shown in Fig. 4.7(a). As the CNT separation distances (2.66 nm) within the nanoscale RVE are within the electron hopping range (3.59 nm) for the height of barrier considered herein (1.5 eV), the electrical tunneling effect is turned on along with the inherent piezoresistivity of the CNT. Clear tunneling paths (Fig. 4.7(a)) are formed among the CNTs, and are evolving with the applied strain field along with the inherent piezoresistivity of the CNT. The mesoscale RVE for scenario 2 is illustrated in Fig. 4.7(b), in which there are 849 randomly chosen subelements containing the 62.5%vol nanoscale RVE. The nanoscale RVE for scenario 3 is chosen to be the same as in scenario 2, and the mesoscale RVE for scenario 3 is illustrated in Fig. 4.7(c). It can be seen that for the total 849 subelements containing the nanoscale RVE, 800 subelements are stacked into 20 columns, with the remaining 49 subelements randomly dispersed into the remaining region.

Following the bottom-up algorithm, the effective mechanical properties of the mesoscale RVE for scenarios 2 and 3 are first obtained. For demonstration purposes, the effective mechanical properties with random oriented nanoscale RVE are summarized in Table 4.3. The mechanical properties of the pure polymer matrix are also listed in Table 4.3 for comparison purposes. It is of interest to notice that for scenarios 2 and 3, in which the local CNTs are agglomerated, the effective mechanical properties are very close to the pure polymer matrix. For example, the effective Young's modulus E_{33}^{eff} is only improved by 6.9%, 7.8%, and 10% respectively for the cases of S2, S3 (10 columns), and S3 (20 columns). This is because the effective mechanical properties are the volume averaged values in terms of energy homoge-





Figure 4.7: The 3D multiscale model for scenarios 2 and 3. a) Illustration of the 62.5%vol nanoscale RVE under the transformed mesoscale strain of $\varepsilon' = R\varepsilon R^{-1}$, in which R can be found in Ref. [36] (Displacement magnification factor: 68). b) Illustration of the 1%wt mesoscale RVE with well-dispersed, randomly oriented, and 62.5%vol nanoscale RVEs for scenario 2. c) Illustration of the 1%wt mesoscale RVE with partially dispersed and partially columned, randomly oriented, and 62.5%vol nanoscale RVEs for scenario 3.

nization. Even though the local mechanical properties can be greatly improved due to CNT agglomeration, their influence on the overall effective mechanical properties is limited by the volume averaging process. What can also be noticed in Table 4.3 is that compared to the cases of S3 (10 columns) and S3 (20 columns), the S2 case has better performances in κ_{12}^{eff} , μ_{12}^{eff} , μ_{13}^{eff} , while a poorer performance in E_{33}^{eff} . This is because although well dispersion can help improve the overall mechanical properties in any directions, stacking of CNTs can help better improve the mechanical properties in the particular stacking direction of the CNTs.

Having solved the mechanical problem by using the bottom-up algorithm, similar as in scenario 1, the macroscale strain field ($\tilde{\varepsilon}_{33} = 0\%$ to $\pm 1\%$, $\tilde{\varepsilon}_{11} = -\nu_{31}^{\text{eff}}\tilde{\varepsilon}_{33}$, $\tilde{\varepsilon}_{22} = -\nu_{32}^{\text{eff}}\tilde{\varepsilon}_{33}$) is applied to the cubic mesoscale RVE by using the top-down algorithm through 10 equally increased load steps. For scenario 2, as seen in Fig. 4.8, it is found that with the change of macroscale strain $\tilde{\varepsilon}_{33}$, there is no relative change of effective resistivity ρ_{33}^{eff} of the mesoscale

Table 4.3: The effective mechanical properties of the mesoscale RVE for scenarios 2 and 3 (Unit: GPa). Note that the nanoscale RVE is randomly oriented for all of the 849 subelements.

Scenarios	$\kappa_{12}^{\rm eff}$	$\mu_{12}^{\rm eff}$	$\mu_{13}^{\rm eff}$	$\mathbf{E^{eff}_{33}}$	$\nu_{31}^{\rm eff}$
S2	3.644	1.478	1.479	3.848	0.295
S3 (10 Columns)	3.619	1.467	1.475	3.879	0.296
S3 (20 Columns)	3.596	1.452	1.466	3.965	0.297
Scenarios	$\mathrm{E}^{\mathrm{eff}}$	$ u^{\mathrm{eff}}$			
Pure Polymer	3.600	0.300			

RVE for any orientations of the nanoscale RVE¹. This is because for this dispersion scenario, as there is no percolating conductive paths formed with the mesoscale RVE, the local piezoresistive response of the CNTs can not be transferred to the upper scales. The zerostrain effective resistivities $\rho_{33(0)}^{\text{eff}}$ and tensile and compressive effective gauge factors ($G_{33}^{\text{eff}(T)}$ and $G_{33}^{\text{eff}(C)}$) of the mesoscale RVE for scenario 2 are summarized in Table 4.4. It can be seen that as there is no percolating conductive paths, the zero-strain effective resistivities $\rho_{33(0)}^{\text{eff}}$ for vertical and transverse orientations are both $6.19 \times 10^{14} \ \Omega \cdot m$, which are close to the insulating polymer matrix. The tensile and compressive gauge factors are all 1.6, which are entirely from the geometric effect of the nanocomposites.

For scenario 3, the relative changes of effective resistivity ρ_{33}^{eff} of the mesoscale RVE with the change of macroscale strain $\tilde{\varepsilon}_{33}$ are shown in Fig. 4.8, and the zero-strain effective resistivities $\rho_{33(0)}^{\text{eff}}$ and tensile and compressive effective gauge factors ($G_{33}^{\text{eff}(T)}$ and $G_{33}^{\text{eff}(C)}$) of the mesoscale RVE for different cases are summarized in Table 4.5. It is found that as long as there is percolating conductive paths within the mesoscale RVE, the local nanoscale orientations of the CNT can have a big influence on the macroscale effective gauge factors. For example,

¹The relative change of ρ_{33}^{eff} is in the fifth decimal point after zero, therefore is small enough to be considered as zero.

Table 4.4: The zero-strain resistivities $\rho_{33(0)}^{\text{eff}}$ (Unit: $\Omega \cdot \mathbf{m}$), tensile gauge factors $\mathbf{G}_{33}^{\text{eff}(\mathbf{T})}$, and compressive gauge factors $\mathbf{G}_{33}^{\text{eff}(\mathbf{C})}$ of the mesoscale RVE for scenario 2. Note that the gauge factors are computed at $\tilde{\varepsilon}_{33} = 1\%$.

Orientation	$ ho_{33(0)}^{ m eff}$	$G_{33}^{e\!f\!f(T)}$	$G_{33}^{\rm eff(C)}$
Vertical	6.19×10^{14}	1.6	1.6
Transverse	6.19×10^{14}	1.6	1.6
Pure Polymer	1.0×10^{15}	1.6	1.6

when the nanoscale RVEs are randomly oriented in the transverse $X_1 - X_2$ plane, as illustrated in Fig. 4.9a, the nanoscale CNT tunneling paths become important constituent of the mesoscale percolating conductive paths. Therefore the local nanoscale electrical tunneling effect can be greatly transferred to the upper scales to yield large magnitude gauge factors of ~160 and ~80 respectively for tensions and compressions. As a comparison, when the nanoscale RVEs are vertically oriented in X_3 direction, as illustrated in Fig. 4.9c, the material is electrically saturated by the inherent resistivity (and piezoresistivity) of the CNT, therefore the macroscale piezoresistivity is entirely from the inherent piezoresistivity of the CNT, which is much smaller than the electrical tunneling effect, and are of 10 in both tensions and compressions. For the other orientation cases, as illustrated in Fig. 4.9c, the piezoresistive response of the mesoscale RVE is originated from a combination of the electrical tunneling effect and the inherent piezoresistivity of the CNT, and the effective gauge factors can vary in a large range depending on the local nanoscale orientations.

It is also of interest to see that for both of the transverse and vertical cases, while the effective resistivity ρ_{33}^{eff} of the mesoscale RVE with 10 columns is approximately twice of the mesoscale RVE with 20 columns (Table 4.5), which satisfies the rule of mixtures, their relative changes of resistivity ρ_{33}^{eff} are nearly the same, as observed in Fig. 4.8. For the vertical orientation, the mesoscale RVE with 10 columns and 20 columns both yield effective tension and compression



Figure 4.8: The relative change of effective resistivity $\Delta \rho_{33}^{\text{eff}} / \rho_{33(0)}^{\text{eff}}$ of the mesoscale RVE when the macroscale strain $\tilde{\varepsilon}_{33}$ is from 0% to $\pm 1\%$ for scenarios 2 and 3.



Figure 4.9: Illustration of the different combination of orientations of the nanoscale RVE within the columns of the mesoscale RVE. a) Random orientation in the transverse $X_1 - X_2$ plane. b) Random orientation in the 3D space. c) Vertical orientation in X_3 direction.

gauge factors of 10, and for the transverse orientation, they both yield effective tension and compression gauge factors of ~ 160 and ~ 80 respectively. The results imply that although the number of percolating conductive paths can influence the magnitude of effective resistivity of the CNT-polymer nanocomposites, the piezoresistive response of the material is more from the multiscale architecture of the conductive paths, instead of the number of conductive paths.

Table 4.5: The zero-strain resistivities $\rho_{33(0)}^{\text{eff}}$ (Unit: $\Omega \cdot \mathbf{m}$), tensile gauge factors $G_{33}^{\text{eff}(T)}$, and compressive gauge factors $G_{33}^{\text{eff}(C)}$ of the mesoscale RVE for scenario 3. Note that the gauge factors are computed at $\tilde{\varepsilon}_{33} = 1\%$.

Orientation	$ ho_{33(0)}^{ m eff}$	$G_{33}^{\mathrm{eff}(\mathrm{T})}$	$G_{33}^{\rm eff(C)}$
10 Columns+Vertical	2.82×10^{-3}	10	10
20 Columns+Vertical	1.42×10^{-3}	10	10
10 Columns+Transverse	1.37×10^{12}	158	81
20 Columns+Transverse	6.93×10^{11}	156	80
Pure Polymer	1.00×10^{15}	1.6	1.6

Besides, what can also be observed from Fig. 4.8 is that when the nanoscale RVEs are transversely oriented, the piezoresistive response of the mesoscale RVE shows tension/compression asymmetry, with the tensile piezoresistive response larger than the compressive piezoresistive response. As seen in Table 4.5, the tensile gauge factors $\tilde{G}_{33}^{\text{eff}(T)}$ at $\tilde{\varepsilon}_{33} = 1\%$ are approximated twice of the compressive gauge factors $\tilde{G}_{33}^{\text{eff}(C)}$ at $\tilde{\varepsilon}_{33} = -1\%$. This is because when the nanoscale RVEs are transversely oriented, the electrical tunneling effect becomes the dominant mechanism. The governing equation of the electrical tunneling effect (Ren and Seidel, 2013b) is found to have strong tension/compression asymmetry, such that the magnitude of relative change of resistivity at tension can be much larger than the magnitude of relative change of resistivity at compression. Therefore, the overall piezoresistive response of the CNT-polymer nanocomposites is reflective of the nanoscale electrical tunneling effect and shows tension/compression asymmetry.

4.4 Conclusions

By using a 3D multiscale piezoresistive model, the CNT dispersion effect on the macroscale piezoresistive response of the CNT-polymer nanocomposites is studied. It is found that well dispersion and no local agglomeration of the CNTs can greatly improve the macroscale effective mechanical properties of the CNT-polymer nanocomposites. However, as the CNT distances are larger than the critical tunneling distance for electrons to hop from one CNT to another, the electrical tunneling effect is not active. In order for the macroscale nanocomposites to have a piezoresistive response different from pure geometric effect, it needs two conditions: 1) there is inherent piezoresistivity of the CNT and 2) the material is electrically percolated by the CNT network. On the other hand, although it is found that local agglomeration of the CNTs can be of limited help in improving the macroscale effective mechanical properties, as the CNTs are within the critical tunneling distance, the electrical tunneling effect can be active. Through the electrical tunneling effect, the gauge factors of the CNT-polymer nanocomposites shows tension/compression asymmetry, with the tensile gauge factors much larger than compressive gauge factors.

It is know that the real CNTs are of finite length, therefore in the CNT-polymer nanocomposites it is hard for the CNTs to directly connected and perfectly bounded to each other from tip to tip to form a percolating conductive paths. Therefore, from the modeling work, it is believed that the CNT-polymer nanocomposites' macroscale piezoresistive response is more likely from a combination of the electrical tunneling effect and the inherent piezoresistivity of the CNT, with the former being the dominant mechanism. The modeling work further shows that the complication and variation of CNT dispersions is one important reason for the piezoresistive gauge factors of the CNT-polymer nanocomposites varying in such a big range as found in the literature. Therefore, it is necessary to control the micro and nano dispersions of the CNTs for obtaining large and consistent macroscale gauge factors and further for the CNT-polymer nanocomposites' better use in structural health monitoring
Xiang Ren

applications.

Modeling of Electrostatic Properties of Fuzzy Fiber Reinforced Polymer Composites via Hierarchical Composite Cylinders Method

5.1 Introduction

Since the introduction by Hashin and Rosen (1964), analytic composite cylinders methods (CCM) have been widely used to obtain the effective elastic, thermoelastic, and electrostatic properties of materials with cylindrical inclusions (e.g. structural fibers) (Hashin and Rosen, 1964; Christensen and Lo, 1979; Hashin, 1990; Seidel and Lagoudas, 2006, 2009; Tsukrov and Drach, 2010; Chatzigeorgiou et al., 2012). In the CCM models, aligned fiber reinforced polymer composites can be idealized into concentric cylindrical layers, with each layer accounting for different phases of the composites. The hierarchical CCM model introduced here is based on the traditional CCM, which, however, has been modified to take into ac-

count the radial symmetry of the fuzzy fiber interphase region by introducing a nanoscale electrostatic CCM model. The results are compared with the ones obtained from a similar hierarchical finite element model, and good agreement is found between the two models. The obtained effective electrostatic properties are used as initial analytic solutions for the fuzzy fiber reinforced polymer composites without the electrical tunneling (electron hopping) effect (Simmons, 1963; Li et al., 2007; Ren and Seidel, 2013b) within the polymer matrix.

5.2 Hierarchical CCM Modeling for Electrostatic Properties of Fuzzy Fiber Reinforced Polymer Composites

A fuzzy fiber reinforced polymer composite material system is a fiber composite (Fig. 5.1a), in which some or all of the structural fibers (glass fibers) are coated with radially aligned microfibers (multi-walled carbon nanotubes (MWCNTs)) (Fig. 5.1b). For modeling purposes we assume (Chatzigeorgiou et al. (2012)) that the representative volume element (RVE) of the fuzzy fiber contains three layers: the first layer is the cylindrical glass fiber. The second is a reinforced nanocomposite interphase (intermediate cylindrical layer) which consists of cylindrical MWCNTs and matrix. The third layer is the area of the pure matrix (Fig. 5.1b). The coated glass fibers are arranged to correspond to a unidirectional lamina layer (Fig. 5.1a), in which the fibers are aligned in the z direction and are well dispersed (randomly distributed) in the x - y plane. The fibers and the matrix are either isotropic, or transversely isotropic linearly elastic materials with the axis of symmetry parallel to the axis of the fibers. The MWCNTs in the reinforced nanocomposite interphase are assumed to be transversely isotropic with the axis of symmetry parallel with the MWCNT axis (r-direction in Fig. 5.1b). The idealized RVE of the reinforced interphase is shown in Fig. 5.1c.

Based on the observations that (a) the diameter of the glass fiber is very large compared to the

diameter of the MWCNTs and (b) the MWCNTs are normally densely packed along the glass fiber surface (small $\Delta \theta$ in Fig. 5.1c), we can assume that the reinforced interphase behaves as a classical unidirectional composite (Fig. 5.1d), and effectively it is a transversely isotropic medium with the axis of symmetry parallel to the axis of MWCNTs (i.e. in the radial direction of the glass fiber). Hence, we can use micromechanics methods for composites with aligned microfibers in determining the transversely isotropic interphase properties (Seidel and Lagoudas (2006)).

The effective electrostatic properties of the aligned fuzzy fiber reinforced polymer composites can be obtained by using CCM model in which the second layer is the interphase region. In order to simplify the problem, let us likewise assume the CNTs in the interphase region are of the same length, homogeneously distributed, straight and radially oriented, with perfect bounding to the glass fiber and matrix, as illustrated in Fig. 5.1. As an initial study, we will disregard the effects of electron hopping. The electrostatic properties of the structural fibers and the polymer matrix can be considered as homogeneous and isotropic, but what makes a difference is the interphase region, whose electrostatic properties are of anisotropic symmetry if denoted in rectangle Cartesian coordinate system, such that the analytic solutions are hard to find. However, by observing the CNTs are radially oriented, it is convenient to denote the effective electrical conductivities of the interphase region as cylindrically orthotropic in Cylindrical coordinate system, whose three components are $\kappa_{\rm rr}^{(2)}$, $\kappa_{\theta\theta}^{(2)}$, and $\kappa_{\rm zz}^{(2)1}$, in which (2) denotes the conductivities in the second layer. Further, if we introduce a nanoscale RVE to represent a small area of the interphase region (Fig. 5.1c), we can consider the densely packed CNTs on the glass fiber to have periodic hexagonal pattern in every local nanoscale area (Fig. 5.1d), which implies that the interphase region in the nanoscale can be regarded as transversely isotropic, with the axial direction in the radial direction relative to the glass fiber.

¹In the fuzzy fiber interphase region, due to the curvature of the glass fiber surface, the volume fraction of the CNT is actually radially dependent, with the volume fraction higher close to the glass fiber and lower farther away from it. However, considering the CNTs are densely-packed, the dependency is very weak, which is therefore omitted and the volume fraction of the CNT is kept as the one in the middle of the interphase.



Figure 5.1: Schematic of (a) a cross-ply laminate with mixture of non-fuzzy and fuzzy glass fibers, (b) individual fuzzy fiber corresponding to the composite cylinder model (representative of an aligned all fuzzy fiber laminate plies), with the first (innermost) layer being the structural glass fiber, the second layer being the nanocomposite interphase where there are densely packed and radially oriented CNTs, and the third layer being the pure polymer matrix, (c) $\Delta\theta$, Δr , and Δz segment of the nanocomposite interphase region, (d) well-dispersed, densely packed CNTs within the interphase corresponding to a hexagonal packing originating at the glass fiber-nanocomposite interface (the hat denotes local MWCNT scale), (e) nanocomposite composite cylinders model.

Therefore we can use the nanoscale CCM model to get the effective electrical conductivities of the nanoscale first (Fig. 5.1e), and then relate the nanoscale effective properties with those of the microscale, such that

$$\kappa_{rr}^{(2)} = \hat{\kappa}_{zz}^{(2)\text{eff}} \quad \text{and} \quad \kappa_{\theta\theta}^{(2)} = \kappa_{zz}^{(2)} = \hat{\kappa}_{rr}^{(2)\text{eff}} = \hat{\kappa}_{\theta\theta}^{(2)\text{eff}}$$
(5.1)

in which [^]denotes materials properties in the nanoscale.

Once the electrostatic properties of the second layer are obtained, the electrostatic properties for the three layers as identified in Fig. 5.1b are all known. Therefore the electrostatic properties of the microscale can be obtained by using the microscale CCM model, which can be used to represent the electrostatic properties of the fuzzy fiber reinforced composites. Section 5.2.1 introduces the governing equations for a general electrostatic CCM model, which can be applied either in the nanoscale or microscale.

5.2.1 The governing equations for the electrostatic CCM model

For each layer of the multi-layer cylinder, the steady state conservation of charge equation can be denoted in Cylindrical coordinate system as:

$$\frac{\partial J_r^{(k)}}{\partial r} + \frac{1}{r} \frac{\partial J_\theta^{(k)}}{\partial \theta} + \frac{\partial J_z^{(k)}}{\partial z} + \frac{1}{r} J_r^{(k)} = 0$$
(5.2)

where $J_i^{(k)}$ $(i=r,\theta,z)$ is the current density component with (k) denoting the index of the layer (e.g. k=1 denotes the innermost layer, and so on). Similarly, for the homogenized effective material, the (k) in (5.2) can be replaced with the superscript 'eff', where J_i^{eff} $(i=r,\theta,z)$ is the current density component of the effective material. For each layer of the multi-layer cylinder, the electric field component $E_i^{(k)}$ can therefore be denoted with

$$E_r^{(k)} = -\frac{\partial \Phi^{(k)}}{\partial r}, \quad E_{\theta}^{(k)} = -\frac{1}{r} \frac{\partial \Phi^{(k)}}{\partial \theta}, \quad E_z^{(k)} = -\frac{\partial \Phi^{(k)}}{\partial z}$$
(5.3)

where $\Phi^{(k)}$ is the electric potential for each layer of the multi-layer cylinder, and where the (k) can again be suitably replaced for the effective material equations. The current density is related to electric field by Ohm's law which for the multi-layer cylinder can be written as

$$\begin{cases} J_r^{(k)} \\ J_{\theta}^{(k)} \\ J_z^{(k)} \end{cases} = \begin{bmatrix} \kappa_{rr}^{(k)} & 0 & 0 \\ 0 & \kappa_{\theta\theta}^{(k)} & 0 \\ 0 & 0 & \kappa_{zz}^{(k)} \end{bmatrix} \begin{cases} E_r^{(k)} \\ E_{\theta}^{(k)} \\ E_z^{(k)} \end{cases}$$
(5.4)

where $\kappa_{ij}^{(k)}$ denote components of the second order electrical conductivity tensors for each layer of the multi-layer cylinder, where the layers are generally considered as cylindrically

orthotropic such that $\kappa_{rr}^{(k)}$, $\kappa_{\theta\theta}^{(k)}$, and $\kappa_{zz}^{(k)}$ are not necessarily equal. Similarly, for the effective material, Ohm's law can be written as $J_i^{\text{eff}} = \kappa_{ij}^{\text{eff}} E_j^{\text{eff}}$ where κ_{ij}^{eff} denotes the effective conductivities for the effective material, which are obtained by solving electrostatic boundary value problems (BVPs) and constructing electrostatic energy equivalence between the multi-layer cylinder and the effective material. It is noted that, given the cylindrical geometry and cylindrically orthotropic layer conductivities, the effective conductivity should at most maintain the cylindrically orthotropic material symmetry. However, by assuming the fibers are infinitely long and by observing the well-dispersed and aligned fibers have hexagonal symmetry in the transverse plane, the effective electrostatic material properties can be considered as transversely isotropic (Hashin and Rosen (1964)). Therefore, $\kappa_{rr}^{\text{eff}} = \kappa_{\theta\theta}^{\text{eff}}$, and as such, only two BVPs are then needed (one axial and one transverse) to obtain the two unknown effective electrostatic properties, which are introduced as below.

The in-plane electrostatic BVP

The electric potential for each layer of the multi-layer cylinder is:

$$\Phi^{(k)} = (A^{(k)}r^{\sqrt{\frac{\kappa_{\theta\theta}^{(k)}}{\kappa_{rr}^{(k)}}}} + B^{(k)}r^{-\sqrt{\frac{\kappa_{\theta\theta}^{(k)}}{\kappa_{rr}^{(k)}}}})\cos(\theta)$$
(5.5)

where $\kappa_{rr}^{\mathbf{k}}$ and $\kappa_{\theta\theta}^{\mathbf{k}}$ are known conductivities of each layer, and $A^{(k)}$ and $B^{(k)}$ are unknown constants to be solved by using boundary conditions and matching conditions. It is worth noticing that for a layer with in plane isotropic electrostatic properties, i.e. $\kappa_{rr}^{(k)} = \kappa_{\theta\theta}^{(k)}$, the power terms in (5.5) are reduced to one. This is the case not only for the isotropic glass fiber and matrix materials of the composite cylinder assemblage, but also for the effective homogeneous cylinder which is transversely isotropic with r- θ isotropy plane. However, for the interphase region of the fuzzy fiber which is cylindrically orthotropic such that $\kappa_{rr}^{(2)} \neq \kappa_{\theta\theta}^{(2)}$, the power terms are not equal to one. As the adjacent layers of the multi-layer cylinder are assumed to be perfectly bounded, the matching conditions between adjacent layers are:

$$\Phi^{(k)}(r=r_k) = \Phi^{(k+1)}(r=r_k), \quad k=1 \text{ to } N-1$$
(5.6a)

$$J^{(k)}(r = r_k) = J^{(k+1)}(r = r_k), \quad k = 1 \text{ to } N - 1$$
(5.6b)

in which N denotes the total number of layers. The boundary conditions for the multi-layer cylinder are:

$$\Phi^{(N)} = E_0 r \cos(\theta) \mid_{r=r_N, 0 \le z \le L}$$
(5.7a)

$$\Phi^{(1)} = 0 |_{r=r_0=0, 0 \le z \le L} \text{ or } J^{(1)} = 0 |_{r=r_0 \ne 0, 0 \le z \le L}$$
(5.7b)

in which E_0 is a constant electric field component associated with a uniform homogeneous electric field at the macroscale (i.e. here the laminate layer scale), L is the length of the CCM model in z-direction, and r_0 and r_N are the innermost and outermost radius, respectively, of the multi-layer cylinder. Specifically, if $r_0 = 0$, the innermost layer is solid and the first condition of (5.7b) is applied such that $B^{(1)} = 0$ so that the potential solution remains bounded. In contrast, if $r_0 \neq 0$, there is a hollow region in the innermost layer, and the second condition in (5.7b) is applied. Similarly, the boundary conditions for the effective homogeneous solid cylinder material are giving (5.7a) and the first of (5.7b) with superscripts (N) and (1) replaced by 'eff'.

The axial electrostatic BVP

The electric potential for each layer of the multi-layer cylinder is:

$$\Phi^{(k)} = A^{(k)}z + B^{(k)} \tag{5.8}$$

where $A^{(k)}$ and $B^{(k)}$ are unknown constants to be solved by using boundary conditions. The boundary conditions of the multi-layer cylinder are provided as

$$\Phi^{(k)}|_{z=0} = \Phi_0 \ (k = 1 \text{ to } N) \tag{5.9a}$$

$$\Phi^{(k)}|_{z=L} = \Phi_1 \ (k = 1 \text{ to } N) \tag{5.9b}$$

in which Φ_0 and Φ_1 are constant potentials as applied at z = 0 and z = L respectively. It is noted that, as there is no r- or θ -dependence in the electric potential, then there is no need to enforce matching conditions between the layers. The effective homogeneous solid cylinder is subject to the same form of the potential and boundary conditions as in (5.8) and (5.9).

Electrostatic energy equivalence

For each BVP, volume averaged electrostatic energy equivalence is constructed between the multi-layer cylinder and the effective material, such that $W^{\text{RVE}} = W^{\text{eff}}$ where

$$W^{\text{RVE}} = \frac{1}{V} \sum_{k=1}^{N} \int_{0}^{L} \int_{0}^{2\pi} \int_{r_{k-1}}^{r_{k}} \frac{1}{2} E_{i}^{(k)} J_{i}^{(k)} r dr d\theta dz$$
(5.10a)

$$W^{\text{eff}} = \frac{1}{V} \int_0^L \int_0^{2\pi} \int_0^{r_N} \frac{1}{2} E_i^{\text{eff}} J_i^{\text{eff}} r dr d\theta dz$$
(5.10b)

in which V is the whole volume of the model and $V = \pi r_N^2 L$. For the in-plane BVP, $W^{\text{eff}} = \frac{1}{2} E_0^2 \kappa_{rr}^{\text{eff}} = \frac{1}{2} E_0^2 \kappa_{\theta\theta}^{\text{eff}}$ and for the axial BVP, $W^{\text{eff}} = \frac{1}{2} E_0^2 \kappa_{zz}^{\text{eff}}$. However, it is noted that the effective properties resulting for the equating (5.10a) and (5.10b) are independent of the magnitude of the applied electric field as solution of the BVPs reveal that $A^{(k)}$ and $B^{(k)}$ depend linearly on E_0 .

5.3 Examples

In the following examples we consider E glass fibers with radius 5 μ m coated with radially aligned hollow carbon nanotubes. The CNTs we study here are considered to be structured with 5 walls of 0.34nm thickness each. The CNTs have internal radius 0.518 nm and external radius 2.218 nm. The fuzzy fibers are embedded in EPIKOTE 862 resin. The properties of the CNT walls are assumed the same as the properties of the graphene. The electrostatic properties of the glass fibers, the resin and the graphene are shown in Table 5.3. It is noted that when the thicknesses of the nanocomposite interphase are 1 μ m and 2 μ m respectively, the percolation concentrations of fuzzy fiber are 0.69 and 0.51, which are used as upper limits for the volume fraction of glass fiber in the microscale CCM model.

Table 5.1: The electrostatic properties of fuzzy fiber components (Hartman et al. (2006);Ebbesen et al. (1996);Resolution Performance Products (2001)).

E glass fiber	2.49E-13~S/m
EPIKOTE 862 resin	6.7E-7 S/m
Graphene	$1.0\mathrm{E5~S/m}$

The nanoscale CCM model is first used to obtain the effective electrostatic properties of the well-dispersed and aligned CNTs in the polymer matrix, as shown in Table 5.2. It is observed that with the increase of volume fraction of CNTs in the interphase region, the conductivities $\kappa_{rr}^{(2)}$, $\kappa_{\theta\theta}^{(2)}$, and $\kappa_{zz}^{(2)}$ are all enhanced. It is also noticeable that the radial conductivity $\kappa_{rr}^{(2)}$ is 10 orders higher than the values of the other two directions due to the radial alignment of the CNTs in the interphase region.

Table 5.2: The effective conductivities of the fuzzy fiber interphase region as obtained from the nanoscale CCM model, i.e. $\kappa_{rr}^{(2)} = \hat{\kappa}_{zz}^{(2)\text{eff}}$ and $\kappa_{\theta\theta}^{(2)} = \kappa_{zz}^{(2)} = \hat{\kappa}_{rr}^{(2)\text{eff}} = \hat{\kappa}_{\theta\theta}^{(2)\text{eff}}$ (Unit: S/m).

Cases	$1 \ \mu m \&$	$1 \ \mu m \&$	$1 \ \mu m \&$	$2 \ \mu m \&$	$2 \ \mu m \ \&$	$2 \ \mu m \&$
	45.45%	59.09%	72.73%	41.67%	54.17%	66.67%
$\kappa_{rr}^{(2)}$	4.297E4	5.587E4	6.876E4	3.940E4	5.122E4	6.303E4
$\kappa^{(2)}_{\theta\theta} = \kappa^{(2)}_{zz}$	1.778E-6	2.593E-6	4.223E-6	1.619E-6	2.243E-6	3.334E-6

By applying the microscale CCM model, the effective conductivities of the aligned fuzzy fiber reinforced polymer composites can be obtained. When the interphase thickness is 1 μ m, the change of effective axial conductivity κ_{zz}^{eff} of the composites with the change of volume fraction of glass fiber is shown in Fig. 5.2(a). It can be observed that with the increase of volume fraction of glass fiber, the effective axial conductivity of the pure glass fiber reinforced polymer composites become lower due to the glass fiber's low conductivity relative to the matrix. However, with the interphase region added to the surface of glass fiber, the trend is reversed as the axial interphase conductivity begins to exceed that of the matrix with increase in MWCNT concentration. For example, with the volume fraction of glass fiber of

0.51, when the average volume fraction of MWCNTs in the interphase region is increased from 45.45% to 72.73%, the effective axial conductivities of the fuzzy fiber reinforced polymer composites are increased by 76.3%, 132%, and 244%, respectively, compared to the pure glass fiber case. Similar increases can be found in the 2 μ m thickness interphase cases where, at the volume fraction of glass fiber of 0.51, the effective axial conductivities of the fuzzy fiber reinforced polymer composites are increased by 143%, 237%, and 400% for interphase average MWCNT volume fractions of increasing from 41.67% to 66.67%, respectively. These observations are consistent with the three phase rule of mixtures which results from the axial CCM electrostatic BVP. With the thickness of the nanocomposite interphase fixed, as the glass fiber volume fraction increases, so too does the nanocomposite interphase volume fraction, thereby rapidly decreasing the matrix volume fraction. With the axial conductivity of the interphase being an order of magnitude larger than the matrix, the displacement of additional matrix material in moving to the larger interphase thickness leads to substantially larger increases in the effective axial conductivity of the composite.

The change of effective transverse conductivity κ_{rr}^{eff} of the aligned fuzzy fiber reinforced polymer composites with the change of volume fraction of glass fiber is shown in Fig. 5.2b and demonstrates similar trends to those observed in the effective axial conductivity, i.e. increasing conductivity with increasing MWCNT concentration in the nanocomposite interphase. However, despite the transverse conductivity of the nanocomposite interphase, $\kappa_{rr}^{(2)}$, being eight orders of magnitude larger than the axial interphase conductivity, κ_{zz}^{eff} (which is equal to theta transverse conductivity, $\kappa_{\theta\theta}^{\text{eff}}$), the increases in fuzzy fiber reinforced polymer composite effective transverse conductivity are much smaller than those observed for the composite axial conductivity.

In confirming these observations, a comparison of the hierarchical electrostatic CCM model with a finite element model (FEM) based on the 2D microscale hexagonal representative volume elements (RVE) (Hammerand et al. (2007)) is constructed. For the fuzzy fiber's





Figure 5.2: The axial effective conductivity κ_{zz}^{eff} and (b) comparison of the transverse effective conductivity κ_{rr}^{eff} as obtained from CCM and FEM for aligned fuzzy fiber reinforced polymer composites with the change of volume fraction of glass fiber when the interphase thickness is 1 μ m.



Figure 5.3: The change of effective conductivities of the composites with the change of volume fraction of glass fiber/glass fiber core by using the Mori-Tanaka method.

interphase region, the nanoscale electrostatic properties are taken from the nanoscale CCM model and transformed from the Cylindrical coordinate system in the nanoscale to the Cartesian coordinate system in the microscale resulting in θ -dependent interphase conductivities as shown in Fig. 5.4(a). Three electrostatic periodic boundary conditions (PBCs) are independently applied to the microscale RVE, with the energy equivalence method used to

obtain the effective electrostatic properties κ_{11}^{eff} , κ_{22}^{eff} , and κ_{12}^{eff} (Ren and Seidel (2013a)). It is found that κ_{11}^{eff} and κ_{22}^{eff} are equal to each other, and κ_{12}^{eff} is zero, which confirms the accuracy of the transversely isotropic assumption as in the CCM model. As an illustration, the potential, electric field, and current density contours for obtaining κ_{22}^{eff} are shown in Fig. 5.4(b). The transverse effective electrostatic properties as obtained from the FEM model compare well with the CCM model as seen in Fig. 5.2(b), which again confirms the accuracy of the material symmetry assumptions in the hierarchical CCM model.

In contrast to the three-phase rule of mixtures behavior of the axial conductivity, the transverse properties obtained from the CCM and FEM are instead matrix dominated. Yet it is worth noting that relative to the observed changes in the mechanical properties (Seidel et al., 2014), the increases in both the axial and transverse effective fuzzy fiber electrical conductivity are of sufficient significance to be of practical application in making electrically conductive polymers.

For composites with randomly dispersed glass or fuzzy fibers, the Mori-Tanaka method is used to obtain the effective electrostatic properties. As seen in Fig. 5.3, for the composites with randomly dispersed fuzzy fibers, the effective conductivity κ^{eff}_{zz} and the transverse conductivity κ^{eff}_{rr} of the composites is isotropic, and lies between the axial conductivity κ^{eff}_{zz} and the transverse conductivity κ^{eff}_{rr} of the composites with aligned fibers. For the composites with random dispersion of fiber orientations, the effective properties are obtained by averaging the fiber response over all the orientations such that the net isotropic symmetry lies between the contributing bounding values of the local orientation axial and transverse conductivities. Also of note in Fig. 5.3 is that, due dominance of the polymer matrix in the transverse direction, the effective conductivities of the composites with randomly dispersed glass or fuzzy fibers are closer to the effective transverse conductivities as opposed to the effective axial conductivities, thereby indicating the potential importance of controlled placement and alignment of fuzzy fibers in applications.

For the composites with a mixture of aligned glass and fuzzy fibers, as seen in Fig. 5.5(a), even



Figure 5.4: (a) Distribution of electrical conductivities and (b) distribution of electric potential Φ , electric field E_2 , and current density J_2 in the 2D microscale hexagonal RVE when a periodic potential difference of $\Delta \Phi = \hat{E}_0 \cdot W_2$ is applied in Y direction (vertical), in which E_0 is a constant macroscale electric field and W_2 is the width of the 2D microscale RVE in the Y direction. The 2D microscale RVE represents the nanocomposites in which there are 30% glass fibers with a 2 μ m thickness interphase, and the average volume fraction of CNTs within the interphase is 54.17%.

with a small fraction of the glass fibers being fuzzy fibers, the axial effective conductivity κ_{zz}^{eff} of the composite can be significantly increased. However, as seen in Fig. 5.5(b), the transverse effective conductivity κ_{rr}^{eff} of the composites is only marginally influenced by the replacement of pure glass fibers with fuzzy fibers. This indicates not only the importance of controlling alignment of fibers within a composite, but also the level of control over ply properties offered by specifying glass/fuzzy fiber mixture ratios.





Figure 5.5: (a) The change of effective axial conductivity κ_{zz}^{eff} and (b) the change of effective transverse conductivity κ_{rr}^{eff} of composites with volume fraction of glass fiber/glass fiber core. Note: In the mixture of glass and fuzzy fiber cases, the volume fraction reported for fuzzy fiber is the one of the glass fiber core which is kept constant at 10%, 20% and 30%, respectively, while the volume fraction of the pure glass fibers increases from 0-0.6.

5.4 Conclusions

By taking advantage of the cylindrical orthotropic symmetry, analytic hierarchical electrostatic CCM models are developed to obtain the effective electrostatic properties of the

nanocomposites with well dispersed and aligned fuzzy fibers. As a comparison, a FEM model for the electrostatic case is developed, which explicitly account for the anisotropic material properties of the fuzzy fiber interphase region to obtain the material response. It is found that the effective electrostatic properties as obtained from the CCM model and the numerical method are in good agreement, which verifies the accuracy of the hierarchical CCM model. In addition, the Mori-Tanaka model is used to obtain the electrostatic properties of the composites with randomly dispersed fuzzy fibers or with mixtures of aligned fuzzy fibers and structural fibers. From these cases the importance of controlling alignment is observed in the sensitivity of the aligned direction properties to the presence and properties of the nanocomposite interphase in terms of effective electrical conductivity. The analytic hierarchical CCM model therefore shows promise as relatively inexpensive preliminary design tools for fuzzy fiber enriched composite laminates.

Computational Multiscale Modeling and Characterization of Piezoresistivity in Fuzzy Fiber Reinforced Polymer Composites

6.1 Introduction

The fuzzy fiber material (Bower et al., 2000; Thostenson et al., 2002; Zhu et al., 2003; Zhao et al., 2005; Ci et al., 2005; Mathur et al., 2008; Garcia et al., 2008; Sager et al., 2009; Yamamoto et al., 2009, 2012; Wood et al., 2012; Sebastian et al., 2014) is an engineering material that has a carbon, glass, ceramic, or alumina structural fiber core, with dense CNT "forest" coated on the fiber surface, as observed in Fig. 1.1. In the fuzzy fiber reinforced polymer composites (FFRPC), the CNTs on the structural fiber surface form a multifunctional interphase region, which can provide enhanced load transfer, damage resistance, higher thermal and electrical conductivities, and electromechanical coupling in the

form of piezoresistivity.

In this study we are focused on modeling and characterization of the piezoresistive response of FFRPC, which is believed to be governed by the piezoresistive response of the nanocomposite interphase. Currently several mechanisms, which may potentially account for the observed overall piezoresistivity of the nanocomposites, have been identified, for example, the electrical tunneling effect (electron hopping) and the inherent piezoresistive effect of the CNT. In both of the mechanisms, the mechanical and electrostatic properties are one-way coupled, i.e. the mechanical properties can greatly influence the electrostatic properties, but not vice versa. In order to obtain the overall piezoresistive response of the nanocomposites, and in turn the FFRPCs, it is crucial to account for the local piezoresistive response in light of multiple mechanisms, especially given the dependence on dispersion.

To date, modeling efforts in the literature have been focused on obtaining the effective mechanical and electrostatic properties of FFRPC (Kundalwal and Ray, 2011, 2012; Chatzigeorgiou et al., 2012; Seidel et al., 2014). For example, Chatzigeorgiou et al. (2012) applied a hierarchical analytic composite cylinders method (CCM) to obtain the overall effective mechanical properties of the composites reinforced by radially aligned fuzzy fibers. The impact of the CNT length and volume fraction on the overall composite properties is studied. In contrast, Kundalwal and Ray (2011, 2012) used the Mechanics of Materials (MOM) approach and the Mori-Tanaka (MT) method respectively for obtaining the effective mechanical properties of the fuzzy fiber reinforced composites. In (Chatzigeorgiou et al., 2012; Kundalwal and Ray, 2011, 2012), it was found that due to the radial growing of CNTs, the transverse effective properties of this composite are significantly improved. In a similar manner as in (Chatzigeorgiou et al., 2012), Seidel et al. (2014) studied the effective electrostatic properties of FFRPC by using a hierarchial electrostatic CCM model and a finite element model (FEM) respectively. However, to our knowledge, no efforts have been found in the literature for modeling the piezoresistive, i.e. the mechanical-electrostatic coupled response of FFRPC.

In this study, single tow piezoresistive fragmentation testing is conducted for characterization of the piezoresistive response of FFRPC. Correspondingly, a 3D computational multiscale mechanical-electrostatic coupled model is constructed to model the same process. The detailed experimental and modeling work are introduced in section 6.2 and section 6.3 respectively.

6.2 Single Tow Piezoresistive Fragmentation Testing

The fuzzy fiber tows being tested were manufactured in the University of Dayton Research Institute, with glass fiber as the structural fiber core, as seen in Fig. 6.1. Within one fuzzy fiber tow, it is estimated that there are roughly 600 single fuzzy fibers. By measuring multiple places of different fuzzy fiber structural cores in SEM, as shown in Fig. 6.1(c), the diameter of the fuzzy fiber structural core is approximately 6 μ m. On the fuzzy fiber structural cores, densely packed and randomly oriented MWCNTs are observed (Fig. 6.1(b), 6.1(d), 6.1(e)). It is also noticeable in Fig. 6.1(c) that in some regions of the fuzzy fiber surfaces, the CNTs are completely peeled off or sparse which may be due to shipping and handling issues. The thickness of the CNT forest on the fuzzy fibers is hard to determine as it varies along the fiber length and from one fiber to another up to several micrometers. The fuzzy fiber tow is embedded into the dogbone-shaped epoxy specimen for piezoresistive testing. The fabrication process of the specimens is introduced in section 6.2.1.

6.2.1 Specimen Fabrication

Dogbone molds with a gauge section length of 26 mm were created out of Mold Max 60 high heat resistance silicon rubber (Smooth-On), as illustrated in Fig. 6.2. A master specimen was made using a 3D printer and was then covered in the degassed silicon mix. The molds were then allowed to cure overnight at room temperature. When the rubber molds were ready for specimen preparation, a light coating of PTFE Mold Release (Miller-Stephenson)



Figure 6.1: a) Optical image of a single fuzzy fiber tow spread apart by tweezers (Scale bar: 2 cm). b) Field emission SEM (FESEM) image of single fuzzy fibers within the fuzzy fiber tow (Scale bar: 100 μ m). c) SEM image of single fuzzy fibers within the fuzzy fiber tow, on which the CNTs are peeled off (Scale bar: 20 μ m). Note that the diameter of the structural fiber core is measured as 6 μ m. d) FSEM image of a section of a single fuzzy fiber (Scale bar: 2 μ m). e) FESEM image of the CNTs on the fuzzy fibers (Scale bar: 1 μ m).



Figure 6.2: Illustration of placing the fuzzy fiber tow into the dogbone mold.

was applied. One end of a fuzzy fiber tow was covered in a conductive silver epoxy (MG Chemicals) and then attached to a braided copper wire. The fuzzy fiber tow was placed inside of a notch created in the molds (Fig. 6.2), and was then cured for 15 minutes inside a 65°C oven. The notch was then filled with a 5-minute epoxy, and the point where the fuzzy fiber is connected to the copper wire was immersed into the 5-minute epoxy. The epoxy was cured for 5 minutes at room temperature. The same procedure was followed for the other side of the mold. When laying the other end of the fuzzy fiber tow connection it was held taught by hand while the 5-minute epoxy was curing to ensure the fuzzy fiber would remain in a tight axial position throughout the dogbone specimen. The resin used for the composites was Epon 862 resin (Miller-Stephenson) with EPIKURE Curing Agent W (Miller-Stephenson). Epon 862 is a low viscosity Bisphenol F liquid epoxy. The resin was mixed with the curing agent at a ratio of 100:26.4 by weight on a $80^{\circ}C$ stirring plate at 120 rpm for one hour. Once the fuzzy fibers tow inside the silicon molds were ready, the epoxy was poured into the molds and then degassed for 10 minutes. The specimens were placed into the oven to cure at 121°C for four hours. After specimens were cool enough to work with, they were sanded down to an even 1.7 mm thickness, as seen in Fig. 6.3(a) and Fig. 6.3(b). One specimen was broken by tension and was viewed at the fracture surface perpendicular to the tow stretch/axial direction, as seen in Fig. 6.3(c) and 6.3(d). The images show that the polymer matrix not only infuses well into the spacings among the single fuzzy fibers, but also spread apart their relative distances. It is further estimated from Fig. 6.3(c) that the volume fraction of fuzzy fibers within the tow is 3%.

6.2.2 Test Procedure

After the specimens were prepared they were secured into a benchtop tensile test machine fabricated in house, as seen in Fig. 6.4. The tensile machine is equipped with a 500 lbs. capacity load cell (Load Cell Central), powered by a NEMA 17 stepper motor (Lin Engineering). Specimens were tested in accordance with the ASTM 3038 composite-fiber testing

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Chapter 6



Figure 6.3: a) Optical image of the dogbone specimen, within which the fuzzy fiber tow is embedded. b) Close up of the connection between the fuzzy fiber tow and the copper wire through the conductive silver epoxy. c) SEM image of the single fuzzy fibers infused by the polymer matrix within the fuzzy fiber tow region of the dogbone specimen (Scale bar: 50 μ m). d) Close up of the fuzzy fibers infused by polymer matrix (Scale bar: 20 μ m).

standard, pulling the specimen at a rate of 2 mm/min. Resistance measurements were obtained at the same time by using an Agilent E4980A precision LCR meter with a two terminal measurement contact.



Figure 6.4: a) In-house fabricated tensile machine with the dogbone specimen being tested.b) Close up of the dogbone specimen gripped on the tensile machine.

6.3 3D Computational Multiscale Model

A 3D computational multiscale mechanical-electrostatic coupled model is constructed to model the piezoresistive response of FFRPC, such that for every integration point of the microscale fuzzy fiber interphase region, there is a corresponding nanoscale representative volume element (RVE) to model the local composite piezoresistive response. The nanoscale effective electrostatic properties are homogenized by energy equivalence method and substituted back into the microscale. Both of the electrical tunneling effect and the inherent piezoresistivity of the CNT are considered in the nanoscale RVEs. The detailed schematics of the 3D computational multiscale model is introduced in section 6.3.1, and the computational procedures are introduced in section 6.3.2 respectively.

6.3.1 Schematics of the 3D Computational Multiscale Model

To represent the macroscale specimen as introduced in section 6.2, a dogbone-shaped finite element model is constructed, as seen in Fig. 6.5a. The dimensions of the finite element model are kept the same as the one of the macroscale specimen. The homogeneous cylindrical inclusion in the model is used to represent the effective fuzzy fiber tow infused by polymer matrix, and the remaining areas are used to represent the neat polymer matrix. As mentioned before, the fuzzy fiber tow contains approximately $N_f = 600$ single fuzzy fibers, the average diameter of the single fuzzy fiber core is $d_f = 6 \ \mu m$, and the volume fraction of single fuzzy fibers within the fuzzy fiber tow is estimated to be $V_f = 3\%$, therefore the diameter of the homogeneous cylindrical inclusion is calculated as $\sqrt{N_f d_f^2/V_f} = 0.849 \ mm$. As observed in Fig. 6.3(c), the single fuzzy fibers within the fuzzy fiber tow are assumed to be well dispersed, aligned, and have homogeneous material properties in their axial directions, therefore the effective mechanical and electrostatic properties of the fuzzy fiber tow can be assumed to be statistically transversely isotropic, for which the 3D hexagonal-array microscale RVE (Hammerand et al., 2007) with a small thickness is used, as shown in Fig. 6.5b. The



Figure 6.5: Schematics of the computational multiscale model for the dogbone specimen under the single tow fragmentation test. a) The macroscale FEM for the dogbone specimen under the single tow fragmentation test. b) The microscale hexagonal RVE (FEM) for the fuzzy fiber tow infused by polymer matrix. c) A single fuzzy fiber infused by polymer matrix. d) The CNT-polymer nanocomposite interphase of the fuzzy fiber. e) The nanoscale hexagonal RVE for the CNT-polymer nanocomposite interphase of fuzzy fiber (The axis of the CNT is in \hat{Y}_1 direction). Note that $\tilde{}$ on the coordinate system denotes the macroscale whereas the $\hat{}$ denotes the nanoscale, with the microscale denoted with an unmodified X_i coordinate system.

single fuzzy fibers as identified in the microscale RVE (as shown in Fig. 6.5c) can be idealized to contain two concentric layers: the first is the cylindrical structural fiber, and the second is the effective nanocomposite interphase (intermediate cylindrical layer) which consists of densely packed CNTs and polymer matrix, as shown in Fig. 6.5d. Based on the observations that (a) the diameter of the structural fiber is very large compared to the diameter of the CNTs and (b) the CNTs are normally densely packed along the structural fiber surface, we assume that locally the CNTs are well-dispersed and aligned. Hence, we can use a nanoscale hexagonal-array RVE as seen in Fig. 6.5e to determine the local piezoresistive response.

The relationship between the microscale coordinate system and the nanoscale coordinate

system is shown in Fig. 6.6. By using 3-1-2 set of Euler angles¹, the coordinate transformation between the micro and nanoscales can be described by the rotation matrix denoted as

$$\mathbf{R} = \begin{bmatrix} \cos(\theta')\cos(\varphi') & \cos(\varphi')\sin(\theta') & -\sin(\varphi') \\ -\sin(\theta') & \cos(\theta') & 0 \\ \cos(\theta')\sin(\varphi') & \sin(\theta')\sin(\varphi') & \cos(\varphi') \end{bmatrix}$$
(6.1)

Conversely, the rotation matrix from the nanoscale to the microscale is taken as $Q = R^{-1}$. Ideally, the CNTs in the interphase region can be assumed to be radially oriented, corresponding to fuzzy fibers like those of Fig. 1.1(a). In this ideal case the interphase can be considered as cylindrically orthotropic symmetry (Tsukrov and Drach, 2010; Chatzigeorgiou et al., 2012) with $\theta' = \theta$ and $\varphi' = 0$, in which $\theta \in [0, 2\pi)$ is the angle formed by the in-plane direction of the nanoscale RVE to the axis of the corresponding structural fiber, as seen in Fig. 6.5b. Conversely, the CNTs can be assumed to be randomly oriented in the interphase region corresponding to fuzzy fibers like those shown in Fig. 1.1(b). In this case, to represent the statistically randomly distributed CNTs, we choose $\theta' = 2\pi y_1$ and $\phi' = \arcsin(y_2)$, in which y_1 and y_2 are generated from random number generators and $y_1 \in [0, 1)$ and $y_2 \in [-1, 1)$ (El-Rahman, 2009).

6.3.2 Computational Procedures for the 3D Multiscale Model

An in-house multiscale finite element code is developed to model the three scales: the macroscale $\tilde{\mathbf{X}}$, the microscale \mathbf{X} , and the nanoscale $\hat{\mathbf{Y}}$. The effective piezoresistive properties of the effective fuzzy fiber tow within the macroscale FEM is represented by the one of the microscale hexagonal RVE, and for every integration point of the interphase region of the microscale hexagonal RVE, there is a corresponding nanoscale RVE to represent the well-dispersed, aligned CNTs leading to the piezoresistive response at the nanoscale. While the macroscale dogbone model is meshed by 4-node linear tetrahedron elements, the mi-

¹The 3-1-2 set of Euler angles corresponds to $\theta' - \omega' - \varphi'$. The Euler angle of ω' by axis 1 is chosen to be 0 by considering the transversely isotropic symmetry of the nanoscale RVE.



Figure 6.6: Schematic representation of the Euler angles between the microscale and nanoscale coordinate systems.

croscale and nanoscale hexagonal microscale RVEs are meshed by 8-node linear hexahedron elements with 8 integration points. The reason for using the linear tetrahedron elements for the macroscale is that it is easier to use them to mesh the macroscale FEM with a cylindrical inclusion, and the reason for using the linear hexahedron elements for the microscale and nanoscale is that it is easier to use them for applying the periodic boundary conditions (P.B.C.s) on the parallelepiped RVEs.

For the mechanical properties of the multiscale model, as the strains applied in the single tow fragmentation tests are small, the material constituents within the multiscale model are assumed to be linear elastic and are assumed to be perfectly bonded with each other. The effective stiffness tensor of the nanoscale hexagonal RVE $\hat{\mathbf{C}}^{\text{eff}}$ is first obtained from the computational micromechanics method by solving several periodic boundary value problems as introduced in (Hammerand et al., 2007), and is then applied at the integration points of the interphase region of the microscale RVE using the rotation matrix obtained from Eq. (6.1) according to:

$$C_{ijkl}^{int,eff}(\theta',\varphi') = Q_{im}(\theta',\varphi')Q_{jn}(\theta',\varphi')\hat{C}_{mnpq}^{eff}Q_{pk}^{-1}(\theta',\varphi')Q_{ql}^{-1}(\theta',\varphi')$$
(6.2)

in which 'int' denotes 'interphase' and 'eff' denotes 'effective'. By applying the computational

micromechanics method again, this time for the microscale RVE as opposed to the nanoscale, the effective mechanical stiffness tensor of the microscale hexagonal RVE \mathbf{C}^{eff} is obtained and as is noted to have transversely isotropic symmetry corresponding to the effective fuzzy fiber tow region with statistically well-dispersed and aligned single fuzzy fibers, i.e. $\tilde{\mathbf{C}}^{\text{eff}} = \mathbf{C}^{\text{eff}}$.

Having obtained the stiffness of the multiscale model, boundary conditions corresponding to those applied in the experiment are introduced to the macroscale FEM, as shown in Fig. 6.7(a). As the 3D macroscale strain tensor $\tilde{\boldsymbol{\varepsilon}}$ within the effective fuzzy fiber tow region is nearly uniform, the average macroscale strain tensor $\tilde{\boldsymbol{\varepsilon}}^{avg}$ is obtained by volume averaging the strain field components within the fuzzy fiber tow region, and is then applied as a set of periodic boundary conditions to the microscale hexagonal RVE, as shown in Fig. 6.7(b), according to

$$u_{i}(\mathcal{S}_{+X_{j}}) - u_{i}(\mathcal{S}_{-X_{j}}) = d(\mathcal{S}_{+X_{j}}, \mathcal{S}_{-X_{j}}) \frac{\partial \tilde{u}_{i}}{\partial \tilde{X}_{j}}$$
(6.3)

in which $S_{\pm X_j}$ are the opposite surfaces on the microscale RVE and $d(S_{\pm X_j}, S_{\pm X_j})$ is the corresponding distance of the opposite surfaces. Under the macroscale average strain field applied as P.B.C.s, the microscale strain tensor at every integration point of the interphase region of the microscale RVE is further obtained and applied to the nanoscale hexagonal RVE as a set of periodic boundary conditions by matrix rotation, i.e.

$$\varepsilon'_{ij}(\theta',\varphi') = R_{ik}(\theta',\varphi')\varepsilon_{kl}R_{lj}^{-1}(\theta',\varphi')$$
(6.4)

in which R depends on the orientation of the nanoscale RVE relative to the microscale coordinate system, as illustrated in Fig. 6.6. The distribution of von Mises strain² of the nanoscale RVE under the applied microscale strain field can be observed in Fig. 6.7(c), in which the relative locations of the CNTs are changed and the CNTs are strained.

Having obtained the local mechanical response in the nanoscale RVE associated with the macroscale applied mechanical loads via the top down approach, two piezoresistive mechanisms are considered within the nanoscale RVE: 1) the electrical tunneling effect and 2) the

²The von Mises strain is obtained as $\hat{\varepsilon}_v = \sqrt{\frac{1}{2} [(\hat{\varepsilon}_{11} - \hat{\varepsilon}_{22})^2 + (\hat{\varepsilon}_{22} - \hat{\varepsilon}_{33})^2 + (\hat{\varepsilon}_{11} - \hat{\varepsilon}_{33})^2 + 6(\hat{\varepsilon}_{23}^2 + \hat{\varepsilon}_{31}^2 + \hat{\varepsilon}_{12}^2)]}$.



Figure 6.7: The computational multiscale model for the mechanical problem. a) Distribution of von Mises strain $\tilde{\varepsilon}_v$ within the dogbone specimen under tensile tension test. b) Distribution of von Mises strain ε_v within the 3%vol microscale RVE under the macroscale strain field of $\tilde{\varepsilon}^{avg}$. c) Distribution of von Mises strain $\hat{\varepsilon}_v$ within the 60%vol nanoscale RVE under the microscale strain field of $\varepsilon' = R\varepsilon R^{-1}$. Note that in this showing case the CNTs are assumed to be cylindrically orthotropic within the fuzzy fiber interphase region.

inherent CNT piezoresistivity. The electrical tunneling algorithm applied herein within the finite element model has been discussed in detail in our previous work in (Ren and Seidel, 2013b). Applying this algorithm to all matrix points in the well-dispersed nanoscale RVE leads to a clearly visible pattern of tunneling paths within the matrix (Fig. 6.8(a)) for percolated local nanoscale RVE volume fractions, e.g. greater than 50% depending on tunneling parameters, radius of the CNT, and resistivity of the neat polymer matrix without electrical tunneling effect. As a result of the applied periodic boundary conditions on the nanoscale RVE, the local distances between CNTs will change, as such, the local resistivities of the conducting paths are evolved.

The second mechanism is the inherent piezoresistivity of the CNT, which depends on the strains within the CNT. The CNTs are expected to exhibit inherent piezoresistivity such



Figure 6.8: The computational multiscale model for the electrostatic problem. a) Distribution of resistivities in the 60%vol nanoscale RVE as the applied microscale boundary strain is from 0 to $\varepsilon' = R\varepsilon R^{-1}$. Note that the conducting paths or the CNTs can become more or less conductive depending on the loading conditions on the nanoscale RVE. b) Distribution of resistivities in the 3%vol microscale RVE as the applied macroscale boundary strain is from 0 to $\tilde{\varepsilon}_{ij}^{avg}$. Note that in this showing case the CNTs are assumed to be cylindrically orthotropic within the fuzzy fiber interphase region.

that the change in resistivity is related to the strain in the CNT through the piezoresistive strain coefficients as (Ren and Seidel, 2013a)

$$\Delta \hat{\rho}_{ij}^{\rm C} = \hat{\mathbf{g}}_{ijkl}^{\rm C} \hat{\varepsilon}_{kl} \tag{6.5}$$

Here, for simplified demonstration purposes, it is further assumed that $\hat{g}_{1111} = \hat{g}_{2222} = \hat{g}_{3333}$ with all other \hat{g}_{ijkl} being zero. As a result of the applied P.B.C.s on the nanoscale RVE and by assuming perfect bonding, the amount of strain transferred to the CNTs will increase with increase in applied load, especially at higher volume fractions (Ren and Seidel, 2013a). The corresponding change in CNT resistivity due to inherent piezoresistivity of the CNT (as observed in Fig. 6.8(a)) will in turn have influence on the piezoresistive response of the nanoscale RVE.

Once the distribution of resistivities within the nanoscale RVE is obtained, the electrical energy equivalence method (Ren and Seidel, 2013a) is used to obtain the effective electrostatic

properties of the nanoscale RVE, which are then substituted into the integration points of the microscale RVE. The electrical energy equivalence method is then used again to obtain the effective electrostatic properties ρ_{ij}^{eff} of the microscale RVE, which are used to represent the electrostatic properties of effective fuzzy fiber tow within the macroscale FEM, i.e. $\tilde{\rho}_{ij}^{\text{eff}} = \rho_{ij}^{\text{eff}}$. Having completed the top-down mechanical and bottom-up electrical multiscale portions of the multiscale algorithm, the process is repeated on subsequent mechanical load increments to obtain the macroscale piezoresistive response over the complete loading path corresponding to the fuzzy tow experiments. The macroscale effective gauge factor of the fuzzy fiber tow at each load increment can therefore be denoted as (Ren and Seidel, 2013a):

$$\tilde{\mathbf{G}}_{33}^{\text{eff}} = \frac{1}{\tilde{\varepsilon}_{33}^{\text{avg}}} \left(\frac{\rho_{33}^{\text{eff}}(\tilde{\varepsilon}_{33}^{\text{avg}})}{\rho_{33}^{\text{eff}}(0)} \frac{1 + \tilde{\varepsilon}_{33}^{\text{avg}}}{(1 + \tilde{\varepsilon}_{11}^{\text{avg}})(1 + \tilde{\varepsilon}_{22}^{\text{avg}})} - 1 \right)$$
(6.6)

It is worth mentioning that parallel computation techniques are applied to the nanoscale RVEs by using 40 processors in a cluster system running CentOs Linux 5, such that the total running time of the model is significantly reduced. For example, in our model the macroscale FEM contains $\sim 54,000$ tetrahedron elements, and the microscale RVEs with different thicknesses of the interphase contain 16,000 - 21,000 hexahedron elements. Correspondingly, there are 2,500 - 14,000 integration points within the microscale interphase region, with each integration point relates to a nanoscale RVE of 3,100 - 6,200 hexahedron elements. For such a big 3D multiscale problem, the running time of each time step is in the range of 11 minutes to 126 minutes depending on the RVEs used and the fineness of mesh, which is satisfactorily fast.

6.4 Experimental Results and Discussion

During the fabrication process, the resistances of three different specimens are recorded at each processing step, as seen in Fig. 6.9. From step 1 to step 2, a change of resistance is recorded for each specimen after the conductive epoxy lead is fused with the fuzzy fiber tow. The resistances are still on the same order as the original fuzzy fiber tow, which implies that the conductive epoxy leads and the fuzzy fiber tows are well connected. From step 2 to step 3 every specimen shows an appreciable increase in resistance as the liquid epoxy permeates the fuzzy fiber. This is believed to be from a decrease in local nanocomposite volume fraction as the epoxy separates the CNTs. From step 3 to step 4 there is again appreciable change between uncured and cured epoxy, which implies that the curing caused contraction of the polymer matrix and therefore an increase in local nanocomposite volume fractions. From 4 to 5 the measurable increase in resistance in all specimens implies that there is a thermal expansion effect on the resistance of the specimen. At the last step, upon removal of the specimen from the mold and final sanding to uniform thickness, the resistance is again measured and is taken as the zero strain resistance value, \tilde{R}_0 , in determining the experimentally measured gauge factors. It can be noted that for the three different specimens, the zero strain resistances have a noticeable degree of scatter, which is believed to be due to differences in the fuzzy tow nano and micro structures. As a result, the preferred measure of piezoresistive electromechanical coupling is the gauge factor which is obtained from the relative change in resistance of a given specimen under applied load.



Figure 6.9: The record of resistance at successive steps of the fabrication process for the three fuzzy fiber specimens: 1) fuzzy fiber tow in air, 2) fuzzy fiber tow in air with conductive epoxy leads, 3) fuzzy fiber tow infused in epoxy pre cure within the mold, 4) post cure (hot) of the specimen within the mold, 5) post cure (cool) of the specimen within the mold, and 6) post sanding of the specimen out of the mold.

Once the fuzzy fiber specimens are manufactured, they are placed into the tensile machine, with simultaneous resistance and load measured to obtain the piezoresistive responses, as seen in Fig. 6.10. It is found that there is a good correlation between the measured resistance and the applied load, as seen in Fig.s 6.10(a), 6.10(b), and 6.10(c). Fig. 6.10(a) shows good correlation between load and resistance up to the point of brittle failure, Fig. 6.10(b) demonstrates that in low frequency cyclic loadings, there is very little lag in the resistance, and Fig. 6.10(c) demonstrates that there is very little drift in the signal on pause. The correlation between resistance and load implies that there is good piezoresistivity of FFRPC within the fuzzy fiber tow region of the dogbone specimen. Further, in order to obtain the gauge factors of FFRPC, correlation between the measured relative change of resistance and the applied boundary displacement is obtained, as shown in Fig. 6.10(d). Note that the axial strain $\hat{\varepsilon}_{33}^{avg}$ is from interpretation of the average strain on the effective tow with randomly oriented CNTs by using FEM. It is found that for the three different fuzzy fiber dogbone specimens, the gauge factors \tilde{G}_{33} ($\tilde{G}_{33} = \frac{\Delta \tilde{R}/\tilde{R}_0}{\tilde{\varepsilon}_{33}^{avg}}$) are 0.20, 0.13, and 0.09 respectively at $\hat{\varepsilon}_{33}^{avg} = 6\%$.

A total of 19 fuzzy fiber dogbone specimens were fabricated and tested, with their corresponding gauge factors as a function of applied strain during the loading process obtained and averaged as provided in Fig. 6.11. The key observation is that the obtained gauge factors for the specimens are not sensitive to the applied strain level, which implies that the randomly oriented CNTs within the fuzzy fiber interphase region may be in direct contact with one another such that the nanocomposites is electrically saturated with $\rho_{33}^{\text{eff}}(\hat{\varepsilon}_{33}^{\text{avg}}) = \rho_{33}^{\text{eff}}(0)$ as in Eq. (6.6). The piezoresistive response of the specimen is therefore entirely from its geometric effect, which is not sensitive to the level of applied strain.





Figure 6.10: The piezoresistive response of the fuzzy fiber dogbone specimen with applied external loadings. a) Correlation between measured resistance and linear loading, b) Correlation between measured resistance and cyclic loading, c) Correlation between measured resistance and paused loading, d) Correlation between measured relative change of resistance and applied boundary displacement.

6.5 Modeling Results and Discussion

6.5.1 Modeling of FFRPC with Cylindrical Orthotropic or Randomly Oriented CNTs

The macroscale FEM, and the microscale and nanoscale RVEs are constructed based on morphological data obtained from the characterization of the physical specimens. As mentioned before, the thickness of the interphase on the single fuzzy fibers is hard to determine as it varies along the fiber length and from one fiber to another. As such, a parametric study is



Figure 6.11: The average gauge factor of the dogbone specimen at each applied macroscale strain level, for which 19 specimens are used and the error bars correspond to the standard deviations of the data. Note that the axial strain $\tilde{\varepsilon}_{33}^{\text{avg}}$ is again from interpretation of the average strain on the effective tow with randomly oriented CNTs by using FEM.

conducted wherein the thickness of the nanocomposite interphase of the fuzzy fiber is varied from 1 to 2 to 3 μ m. Such thicknesses are consistent with lengths of MWCNTs observed in Fig. 6.1(e) which were observed to be 1 μ m and longer. In order to simplify the problem, the outer and inner diameters of the CNT are chosen to be 13 nm and 4 nm, respectively, as was reported in (Aviles et al., 2012). Under small strain assumptions, the CNT annulus, epoxy, and glass fiber are taken to be isotropic linear elastic, with the Young's modulus and Poisson's ratio of 1100 GPa and 0.14, 3.0 GPa and 0.3, and 78 GPa and 0.22, respectively (Saito et al., 1998; Hartman et al., 2006). The initial isotropic resistivity within the CNT annulus is chosen to be $10^{-5} \Omega \cdot m$ (Ebbesen et al., 1996; Seidel and Lagoudas, 2009), the isotropic resistivity of the glass fiber is $4.02 \times 10^{12} \ \Omega \cdot m$ (Hartman et al., 2006), and epoxy is likewise isotropic with a measured resistivity of $10^{15} \Omega \cdot m$ in the absence of electrical tunneling. Barrier heights for epoxy have been reported to be on the order of $\lambda = 0.5$ - 2.5 eV (Hu et al., 2012), therefore an average value of $\lambda = 1.5$ eV is used here. In the studies of (Chen and Weng, 2007; Theodosiou and Saravanos, 2010) the reported CNT inherent piezoresistive gauge factors are ≤ 7 under small strains, while in contrast, in (Stampfer et al., 2006) the reported CNT inherent piezoresistive gauge factor can be as large as 2900. In this study a CNT inherent gauge factor of 10 will be converted into diagonal isotropic piezoresistive coefficients \hat{g}_{ijkl}^{C} (Ren and Seidel, 2013a) to study its influence on the overall piezoresistive response of FFRPC.



Figure 6.12: The effective mechanical properties of the microscale RVE as obtained from the FEM and CCM methods respectively, in which the volume fraction of the fuzzy fibers is kept at 3%vol and the thickness of the interphase is kept at 2µm for increasing CNT volume fractions in the nanocomposite interphase. Note that 'CO' represents 'cylindrically orthotropic' symmetry of the interphase region, and 'RA' represents 'random' distribution of CNTs within the interphase region. a) The microscale effective in-plain bulk modulus κ_{12}^{eff} . b) The microscale effective axial shear modulus μ_{12}^{eff} . c) The microscale effective in-plain shear modulus μ_{23}^{eff} . d) The microscale effective Young's modulus E_{33}^{eff} . e) The microscale effective axial Poisson's ratio ν_{31}^{eff} . Note that for the microscale effective in-plane shear modulus μ_{12}^{eff} , converged solutions of CCM method for some of the nanoscale volume fractions are not available, therefore are omitted showing here.

By solving five periodic boundary value problems (Hammerand et al., 2007), the mechanical properties of the nanoscale RVEs are obtained first, and are substituted into their corre-

sponding integration points within the interphase region of the microscale RVE. Five periodic boundary value problems are solved again such that the effective mechanical properties of the microscale RVE are obtained. For example, the effective mechanical properties of the microscale RVE with the interphase thickness of 2 μ m and with the volume fraction of the CNT at the nanoscale varying from 50% - 90% are shown in Fig. 6.12. For the FFRPC with cylindrically orthotropic (CO) fuzzy fiber interphases, analytic solutions from the CCM method (Chatzigeorgiou et al., 2012; Seidel et al., 2014) are available and are compared with the FEM method, as seen in Figs. 6.12(a), 6.12(c), 6.12(d), and 6.12(e). It can be seen that for the microscale RVEs with 3%vol fuzzy fibers and an interphase thickness of 2 μ m, the effective properties κ_{12}^{eff} , μ_{23}^{eff} , and ν_{31}^{eff} of the two methods match very well up to 90%vol, with the relative differences of -0.15%, -0.55%, and -0.65% respectively compared to the FEM method. However, for the effective Young's modulus E_{33}^{eff} , the relative difference is -32.4% compared to the FEM method. This big difference is believed to be from the misrepresentation of the geometry at such large volume fractions of the CCM method which continues to represent the matrix as an encompassing concentric cylinder phase.

In contrast, for the microscale RVEs in which there are randomly (RA) oriented CNTs in the interphase region, the mechanical properties are obtained by assigning random orientation of the nanoscale RVEs to the integration points of the interphase region, and then solving five periodic boundary value problems at the microscale. To allow for different sets of random orientations of the CNTs in the interphase region, the code is run 10 times, and it is found that very close effective material properties are obtained for each set of random orientations, with the standard deviation three to six orders smaller. Therefore the RA results presented in Fig. 6.12 are believed to be statistically reasonable. It can be seen that the effective properties κ_{12}^{eff} , μ_{12}^{eff} , μ_{23}^{eff} , and ν_{31}^{eff} of the microscale RVEs with RA interphases are very close to the ones with CO interphases, with the relative differences smaller than 0.1%, 1.3%, 4.0%, and 4.4% respectively compared to the FEM CO results. The key difference is again focused on E_{33}^{eff} , which is increased by 58.1%, 68.2%, 76.4%, 78.0%, and 49.5% respectively compared to the FEM CO results when the volume fraction of the CNT is from 50% to 90% at the
interphase region. This difference arises because by randomly aligning the CNTs within the interphase region, the axial Young's modulus of FFRPC is greatly enhanced due to some of the CNT alignments occurring in the axial direction of the fuzzy fiber tow (as opposed to the radial). By comparing the effective mechanical properties of FFRPC with RA and CO interphases, it can be concluded that the RA orientation of the CNT within the interphase is superior for improving the overall mechanical properties of FFRPC.

Once the mechanical properties of the microscale RVEs are obtained, they are substituted into the effective fuzzy fiber tow region of the macroscale FEM, and the load steps are applied through displacement boundary conditions corresponding to those applied in the experiment. From each applied load increment at the macroscale, the volume averaged strain tensor $\tilde{\varepsilon}_{ii}^{avg}$ of the fuzzy fiber tow region is obtained, and is applied as P.B.C.s to the microscale RVEs to obtain their piezoresistive responses according to the multiscale piezoresistive algorithm. The piezoresistive responses of FFRPC with CO interphases are shown in Fig. 6.13, from which the key observations are: 1) with the same nanoscale volume fraction of the CNT (above the nanoscale percolation concentration), as the thickness of the interphase increases, the overall effective axial resistivity ρ_{33}^{eff} decreases. This is because as the thickness of the interphase increases, it replaces the equivalent amount of non-conducting matrix material, therefore the fuzzy fiber tow can have a larger microscale volume fraction of conducting interphase region such that the axial resistivity is reduced. 2) as the nanoscale volume fraction of the CNT increases, the overall effective axial resistivity decreases by orders of magnitude due to increases in electrical conductivity at the nanoscale associated with increased electron hopping. 3) FFRPC with CO interphases yield very large axial gauge factors, which are ranging from 32.8 to 126.6 at $\tilde{\varepsilon}_{33}^{\text{avg}} = 4\%$. 4) For FFRPC with cylindrically orthotropic interphase, the inherent piezoresistivity of the CNT has negligible effect on the overall piezoresistive response at 60% vol - 80% vol of the CNT. Only when the volume fraction of the CNT increases to 90%, there is a limited influence, as observed in Fig. 6.13(d). This is because although there is inherent piezoresistive effect at 60% vol - 80% vol of the CNT, at the strain levels considered here the inherent piezoresistivity of the CNT only increases the

CNT resistivity by at most 4% which remains 16 to 4 orders of magnitude lower than the matrix resistivity such that changes in matrix resistivity due to electron hopping remain the dominant driver of nanoscale piezoresistive response, particularly in the transverse direction as was observed in (Ren and Seidel, 2013b). In contrast, at 90%vol of the CNT, there is greater strain transfer, therefore a greater inherent piezoresistive effect. More importantly the resistivity of the CNT remains on the same order as the electron hopping induced matrix resistivity, therefore at 90%vol the inherent piezoresistivity of the CNT can have an influence on the overall piezoresistive response of FFRPC. It can be seen that at 90%vol, when the thickness of the interphase increases from 1μ m to 3μ m, the overall gauge factor is increased from 35.5 to 36.4, from 34.1 to 35.0, and from 32.8 to 33.7 respectively.

It is of interest to note that at 60%vol CNT within the interphase region, as observed in Fig. 6.13(a), the gauge factor increases with the increase of thickness of the interphase region, however at the other volume fractions of the CNT, the piezoresistive effect decreases with the increase of interphase thickness. It is also observable that from 60%vol to 90%vol of the CNT, the overall gauge factors reach the highest at 70%vol of the CNT, and gradually decrease from 70%vol to 90%vol of the CNT. These results imply that there is a combination of the CNT volume fraction and the fuzzy fiber interphase thickness that can yield the largest gauge factor of FFRPC, and moreover that the gauge factor of FFRPC can be purposely tuned over a large range.

The piezoresistive responses of FFRPC with randomly aligned CNTs in the interphase region $(2\mu \text{m} \text{ thickness})$ are shown in Fig. 6.14. It is found that when considering only the electrical tunneling effect, for nanoscale CNT volume fractions up to to 80%, the overall resistivity at each volume fraction is nearly unchanged with the applied macroscale strain, i.e. there is almost no observable piezoresistive response beyond that of the geometric piezoresistive response when $\rho^{\text{eff}}(\tilde{\varepsilon}_{33}^{\text{avg}}) = \rho^{\text{eff}}(0)$. This is because the nanoscale RVE uses the high aspect ratio argument such that CNTs span the local axial direction (thickness) of the nanoscale RVE. This means that the transverse electron hopping governed resistivity of the radial oriented cases has to directly compete with the CNT themselves (and their inherent piezore-



Figure 6.13: The piezoresistive response of FFRPC with CO interphases, in which the volume fraction of the CNT within the nanoscale RVE is varied from 60% - 90%, and the thickness of the interphase is varied from 1 μ m to 3 μ m. a) ρ_{33}^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{avg}}$ at 60%vol of the CNT, b) ρ_{33}^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{avg}}$ at 70%vol of the CNT, c) ρ_{33}^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{avg}}$ at 80%vol of the CNT, and d) ρ_{33}^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{avg}}$ at 80%vol of the CNT, and d) ρ_{33}^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{avg}}$ at 80%vol of the CNT, and d) ρ_{33}^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{avg}}$ at 80%vol of the CNT, and d) ρ_{33}^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{avg}}$ at 90%vol of the CNT (Unit: $\Omega \cdot m$). Note that in a), b) and c) as the inherent piezoresistivity of the CNT has negligible effect, the curves are the ones corresponding to the electrical tunneling effect only.

sistivity) for nanoscale RVEs aligned in the fuzzy fiber axial direction. As a result, the CNT conductivity formes saturated conductive paths of at least 4 orders larger than that of the transverse paths. Even with strain the transverse paths are not able to change to comparable level of the CNTs. In fact, only when the nanoscale volume fraction of CNT is 90% can a noticeable non-geometric piezoresistive response be observed, as seen in Fig. 6.14. This is because at this extremely high nanoscale volume fraction, the electrical tunneling effect is strong enough to be comparable with the conductivity of CNT and thus, can have an

influence on the overall piezoresistivity. The effective gauge factors corresponding to these electron hopping only cases are 1.475, 1.467, 1.434, and 14.9, respectively, for volume fractions from 60% to 90%. The decrease in effective gauge factor from 1.475 to 1.434 when the volume fraction of the CNT is from 60% to 80% is due to the fuzzy fiber tow becoming stiffer when the volume fraction of CNT is higher. In contrast, the gauge factor of FFRPC with 90%vol CNT is an order of magnitude larger as it consists of both of the geometric effect and the electrical tunneling effect.



Figure 6.14: The piezoresistive response of FFRPC with interphases of randomly aligned CNTs. Note that the volume fraction of the CNT within the nanoscale RVE is varied from 60% - 90%, and the thickness of the interphase is kept at 2 μ m.

When the inherent piezoresistivity of the CNT is considered along with the electrical tunneling effect, there is a clearly discernible piezoresistive response in the observed effective resistivity of the FFRPC for all nanoscale CNT volume fractions as seen in Fig. 6.14. This can again be attributed to the implementation of the high aspect ratio of the CNTs within the nanoscale RVE and the conductive paths which nanoscale RVEs form within the interphase. For the value of inherent CNT piezoresistive gauge factor applied here (10), the rotated average microscale strain lead to local axial strains on the CNTs which induce measurable changes in the axial CNT conductivity, thereby directly affecting the axial conductive paths formed within the randomly oriented interphase. Correspondingly, the overall piezoresistive effects of FFRPC with 60%vol - 90%vol CNTs are larger compared to the ones without inherent piezoresistivity of the CNT, with the gauge factors of \sim 5.5 for 60%vol - 80%vol

CNTs, and 18.2 for 90%vol CNTs.

6.5.2 Modeling of FFRPC with Sparse Regions of the CNT

So far, we have modeled the FFRPC with CO and RA interphases. By considering only the electrical tunneling effect, which is the main mechanism, it is found that the FFRPC with CO interphases can yield large gauge factors ranging from ~ 30 to ~ 120 . In contrast, although the mechanical properties are improved due to random orientation of the CNT, the FFRPC with RA interphases yield smaller gauge factors of ~ 1.5 to ~ 18 . However, it is found that the gauge factors of FFRPC with RA interphases which better represent the observations in Fig. 6.1(d) and Fig. 6.1(e) are still one order larger than the experimental values obtained here (0.14 on average). The reason for the over prediction of gauge factors may attribute to several FFRPC characteristics that the model has not captured, for example, the sparse regions of CNTs along fuzzy fiber length (Fig. 6.1(c)), the curvature and distribution of different CNT types (Fig. 6.1(e)), the random dispersion of fuzzy fibers within the matrix infused tow (Fig. 6.3(d)), etc. Among all of these factors, what is believed can have the most significant influence on the overall piezoresistive response of FFRPC is the sparse regions of CNTs along the fuzzy fiber length.

Due to processing or handling defects, the CNTs on the fuzzy fibers may be peeled off or form sparse regions, which disrupt the axial conductive paths and cause the material to be nonhomogeneous in the axial direction. As such, to obtain $\tilde{G}_{33}^{\text{eff}}$ for the axially nonhomogeneous FFRPC, it not only requires the CNT distribution information along the entire tow, but also requires computations of the corresponding resistivity and strain distributions, which are very computationally challenging. In order to obtain an estimate of the influence of sparse regions on the gauge factor of the fuzzy fiber tow, a simplified approximation of Xiang Ren

Chapter 6

the gauge factor for the axially nonhomogeneous FFRPC can be denoted as:

$$\tilde{G}_{33}^{\text{eff}} = \frac{\Delta \tilde{R}_{3}^{\text{eff}} / \tilde{R}_{3(0)}^{\text{eff}}}{\tilde{\varepsilon}_{33}^{\text{avg}}} = \frac{(\tilde{R}_{3}^{\text{eff}} - \tilde{R}_{3(0)}^{\text{eff}}) / \tilde{R}_{3(0)}^{\text{eff}}}{\tilde{\varepsilon}_{33}^{\text{avg}}} = \frac{\tilde{R}_{3}^{\text{eff}} / \tilde{R}_{3(0)}^{\text{eff}} - 1}{\tilde{\varepsilon}_{33}^{\text{avg}}}$$
(6.7a)

with

$$\tilde{\mathbf{R}}_{3(0)}^{\text{eff}} = \int_{0}^{\tilde{\mathbf{L}}_{0}} \frac{\tilde{\rho}_{33}^{\text{eff}}(\tilde{\mathbf{X}}_{3}, 0)}{\tilde{\mathbf{A}}_{0}(\tilde{\mathbf{X}}_{3})} \mathrm{d}\tilde{\mathbf{X}}_{3}$$
(6.7b)

$$\tilde{R}_{3}^{\text{eff}} = \int_{0}^{\tilde{L}_{0}} \frac{\tilde{\rho}_{33}^{\text{eff}}(\tilde{X}_{3}, \tilde{\varepsilon}_{ij}(\tilde{X}_{3}))}{\tilde{A}_{0}(\tilde{X}_{3})} \frac{1 + \tilde{\varepsilon}_{33}(\tilde{X}_{3})}{(1 + \tilde{\varepsilon}_{11}(\tilde{X}_{3}))(1 + \tilde{\varepsilon}_{22}(\tilde{X}_{3}))} d\tilde{X}_{3}$$
(6.7c)

in which \tilde{L}_0 and \tilde{A}_0 are the original length and cross-section area of the fuzzy fiber tow, $\tilde{\varepsilon}_{ii}^{avg}$ are the volume averaged strain components within the fuzzy fiber tow region, and the axial resistivity $\tilde{\rho}_{33}^{\text{eff}}$ is taken to depend on both the axial location \tilde{X}_3 and the macroscale strain field at X_3 . In order to show the sensitivity of the overall piezoresistivity of FFRPC to the presence of the sparse regions, a model with simplified assumptions is used. As seen in Fig. 6.15(a), it is assumed that on 99.5% of the fuzzy fiber tow, the CNTs are randomly dispersed and statistically homogeneous, with the macroscale average strain field $\tilde{\varepsilon}_{ij}^{avg}$ of the entire fuzzy fiber tow region applied as homogeneous boundary conditions. The remaining 0.5% is considered as sparse regions and is assumed to be concentrated at one axial location within the tow. The geometry of the 0.5% sparse fuzzy fiber tow region is further assumed to be unchanged with strain, and its resistivity is assumed to be unchanged at 7 $\Omega \cdot m$, which corresponds to 0.5% vol randomly oriented CNTs at the nanoscale. Therefore Eq. (6.7) can be simplified into two sub integrations and the overall piezoresistive responses of FFRPC are obtained, as seen in Fig. 6.15(b). It is found that compared to the FFRPC with randomly oriented CNTs and without sparse regions, with only 0.5% sparse regions the overall resistance is increased by 1 to 2 orders and the overall gauge factor is decreased by 1 to 2 orders, which is comparable to the gauge factors from experiments as shown in Fig. 6.11. Thus it can be seen that the sparse regions are indeed likely to have a big influence on the overall piezoresistive response of FFRPC.



Figure 6.15: The piezoresistive response of FFRPC with CNT sparse regions within the fuzzy fiber interphase region. a) Illustration of the fuzzy fiber tow region of the dogbone specimen, in which there is a CNT sparse region. b) \tilde{R}_3^{eff} vs. $\tilde{\varepsilon}_{33}^{\text{eff}}$ of FFRPC with 0.5% CNT sparse regions. Within 99.5% region of the effective fuzzy fiber tow, the nanoscale volume fraction of the CNTs varies from 60% to 90%. Note that the electrical tunneling effect is the sole nanoscale piezoresistive mechanism for the results shown here.

6.6 Conclusions

The piezoresistive response of FFRPC is characterized by using the single tow piezoresistive fragmentation tests, and at the same time is modeled by using a 3D multiscale piezoresistive model. The experimental work shows that the CNTs on the fuzzy fibers are densely packed and randomly dispersed. Approximately linear piezoresistive effect is observed within the fuzzy fiber tow region, and the gauge factors from the tests are on the average of 0.14. The 3D multiscale piezoresistive modeling work shows that the FFRPC with homogeneous cylindrically orthotropic interphase can theoretically yield very large gauge factors varying from ~ 30 to ~ 120 , and that inherent piezoresistivity of the CNT can have very little influence on the overall piezoresistivity for such a microstructure. On the other hand, although it is found that the mechanical properties are improved due to random orientation of the CNT, the FFRPC with statistically homogeneous random interphase yield smaller gauge factors of ~ 1.5 to ~ 18 . This is because the random oriented CNTs in the interphase can form conducting paths directly, which saturates the conductivity and thereby undermines the

FFRPC piezoresistive response induced by electrical tunneling. However such a dispersion of CNTs within the nanocomposite interphase is very sensitive to the inherent piezoresistivity of the CNT. It is found that both of the FFRPC with cylindrically orthotropic and randomly oriented interphases yield gauge factors much larger than the ones as obtained from our experiments (0.14 on average). By considering other factors that may influence the piezoresistive response of FFRPC, it is found that the sparse regions of the CNT along the fuzzy fiber length can have strong effects on the macroscale gauge factor of FFRPC. In summary, based on the modeling work, it is believed that the reason for the observed small gauge factors not only originates from random dispersion of the CNTs within the fuzzy fiber interphase, but also from some other factors such as the CNT sparse regions along the fuzzy fiber length. Based on these results, we have a better understanding of how to tailor the gauge factors of FFRPC based on nano and microscale architectures such that large, consistent, and predictable gauge factors can be purposely obtained for potential structural health monitoring applications.

Concurrent Multiscale Modeling of Coupling between Continuum Damage and Piezoresistivity in CNT-Polymer Nanocomposites

7.1 Introduction

Researchers have found that the piezoresistive response of the CNT-polymer nanocomposites can be an indicator of damage events within the material (Park et al., 2007; Li and Chou, 2008; Saafi, 2009; Gao et al., 2009a,b; Kim et al., 2010; Alexopoulos et al., 2010; Vadlamani et al., 2012b,a; Cardoso et al., 2012; Heeder et al., 2012). For example, by using doublematrix composite techniques, the carbon fiber fracture events were inherently sensed by the piezoresistive response of CNT-polymer nanocomposites, and it was found that the piezoresistivity of the nanocomposites can well capture the fiber fracture events (Park et al., 2007). Saafi (2009) used wireless cement-CNT sensors for damage detection in concrete structures, and it was found that the carbon nanotube networks can in-situ detect crack initiation and propagation. Vadlamani et al. (2012b) dispersed 0.3%wt-0.5%wt CNTs into epoxy, and through measuring the piezoresistivity of the CNT-polymer nanocomposites they studied the in-situ sensing of nonlinear deformation, damage initiation, and growth within the material. It is therefore very attractive for the CNT-polymer nanocomposites to be directly embedded into vehicle structures to provide internal and in-situ strain and damage sensing, e.g. fuzzy fiber reinforced polymer composites (Sebastian et al., 2014; Ren et al., 2014).

The electrical tunneling (electron hopping) effect is found to be the main driving force for the macroscale piezoresistive response of the nanocomposites. It is a phenomenon that when the CNTs are close enough to the order of nanometers, electrical tunneling paths can form in the polymer matrix among the adjacent CNTs (Li et al., 2007; Ren and Seidel, 2013b). The electrical tunneling effect is not only highly sensitive to the relative distances of the CNTs, but also guarantees the polymer nanocomposites to be electrically percolated at an extremely low loading of the CNT. As damage develops in the polymer matrix, the local electrical tunneling effect can be potentially influenced by the evolution of microcracks and the change of relative distances of the CNT, and it is expected that the macroscale piezoresistive response of the CNT-polymer nanocomposites can capture the lower scale damage events.

Among all the different damage phenomena, continuum damage is known to be an irreversible process, brought about by the nucleation, growth, extension, and coalescence of microcavities or microcracks, which can result in deterioration or full failure of mechanical properties (Murakami, 2012). For fiber reinforced laminates, continuum damage in the polymer matrix can become important as it is usually the precedence of other damage events, such as fiber-matrix debonding and fiber breakage (Barbero and Cortes, 2010). In continuum damage mechanics, modeling the microscale damage is usually through prediction of stiffness reduction, and based on the damage initiation criteria, the continuum damage modeling work in the literature can be categorized into two classes. One is that the damage initiation is related to the strengthes of the material, such as the Christensen's or Hashin's failure criteria (Christensen, 1997, 2007; Hashin and Rotem, 1973; Hashin, 1980; Davila et al., 2005; Maimi et al., 2006; Lapczyk and Hurtado, 2007); another is that the damage initiation is related to the internal state variables, such as Talreja et al.'s work (Asp et al., 1996). After damage is initiated, the damage evolution is usually formed by phenomenological laws that are proposed to be related to fracture toughness or internal state variables based on the dissipation rate of energy (Bazant and Oh, 1983).

To better understand the damage and piezoresistivity coupled mechanisms within the CNTpolymer nanocomposites for SHM applications, a multiscale coupled continuum damage and piezoresistive modeling work is developed. The Christensen's failure criteria are applied to determine the initiation of damage within the polymer matrix, and a phenomenological law is used for damage evolution. Further by introducing the damage variables into the governing equation of the electrical tunneling effect, the one-way coupled continuum damage and piezoresistive response of the CNT-polymer nanocomposites is constructed. The macroscale finite element model and the microscale finite element model based on microscale representative volume elements (RVE) are interacted concurrently to obtain the multiscale piezoresistive response. The detailed modeling work is introduced in section 7.2.

7.2 Model description

7.2.1 Modeling of Continuum Damage and Piezoresistive Effects in the CNT-Polymer Nanocomposites

It is assumed that the continuum damage within the polymer matrix is isotropic. For the microscale, we introduce a scalar damage parameter α such that¹

$$\mathbf{C}_{\alpha}(\mathbf{x}, \mathbf{t}) = \mathbf{C}_{0}(\mathbf{x}, \mathbf{t})(1 - \alpha(\mathbf{x}, \mathbf{t}))$$
(7.1)

in which $\mathbf{C}_0(\mathbf{x}, t)$ is the original undamaged isotropic stiffness matrix, $\mathbf{C}_{\alpha}(\mathbf{x}, t)$ is the damaged stiffness matrix induced by continuum damage, \mathbf{x} is the location within the microscale space domain, and t is time. The damage parameter $\alpha(\mathbf{x}, t)$ can vary across the domain and it is assumed that $\alpha(\mathbf{x}, t) \in [0, 1]$. The Christensen's failure criteria are used for the initiation of continuum damage, which are summarized as below:

For
$$0 \le \frac{\sigma_{\rm T}}{\sigma_{\rm C}} \le 1$$

 $(\frac{1}{\sigma_{\rm T}} - \frac{1}{\sigma_{\rm C}})(\sigma_1 + \sigma_2 + \sigma_3) + \frac{1}{2\sigma_{\rm T}\sigma_{\rm C}}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_1 - \sigma_3)^2] \ge 1$ (7.2a)
For $0 \le \frac{\sigma_{\rm T}}{\sigma_{\rm C}} \le \frac{1}{2}$

$$\sigma_1 \ge \sigma_T \text{ or } \sigma_2 \ge \sigma_T \text{ or } \sigma_3 \ge \sigma_T$$

$$(7.2b)$$

in which $\sigma_{\rm T}$ and $\sigma_{\rm C}$ are the tensile and compressive strengths of the polymer matrix, and $\sigma_{\rm i\,(i=1\,to\,3)}$ are the principle stresses. If the Christensen's failure criteria are not satisfied, in other words, if there is no damage in the material, we assign

$$\alpha(\mathbf{x}, t) = 0 \text{ and } \dot{\alpha}(\mathbf{x}, t) = 0 \tag{7.3}$$

Or if the Christensen's failure criteria are satisfied, not to lose generality, the governing law for the evolution of continuum damage in the polymer matrix is formulated as the functional

¹As the stiffness matrix is assumed to be isotropic, Eq. (7.1) can also be stated as $E_{\alpha}(\mathbf{x}, t) = E_0(\mathbf{x}, t)(1 - \alpha(\mathbf{x}, t))$, in which E denotes Young's modulus.

Xiang Ren

Chapter 7

form below:

$$\dot{\alpha}(\mathbf{x}, \mathbf{t}) = f(\alpha(\mathbf{x}, \mathbf{t}), \varepsilon_e(\mathbf{x}, \mathbf{t}))$$
(7.4a)

with

$$\dot{\alpha}(\mathbf{x}, t) = 0$$
 if $(\alpha(\mathbf{x}, t) = 1 \text{ or } \dot{\varepsilon}_e(\mathbf{x}, t) \le 0 \text{ or } \varepsilon_e(\mathbf{x}, t) \le 0)$ (7.4b)

Eq. (7.4a) indicates that the rate of post-failure damage at a specific location depends on the damage that has already been induced and the equivalent strain $\varepsilon_e(\mathbf{x}, t)$. Eq. (7.4b) indicates that 1) if the damage has already been fully developed, i.e. if $\alpha(\mathbf{x}, t) = 1$, there would be no further damage; or 2) if the rate of equivalent strain $\dot{\varepsilon}_e(\mathbf{x}, t)$ goes non-positive, which represents the material is less deformed, there would be no further damage; or 3) if the equivalent strain $\varepsilon_e(\mathbf{x}, t)$ goes non-positive, which represents the material is under compression, there would also be no further damage. In this study we assume the evolution of damage is volumetric such that $\varepsilon_e(\mathbf{x}, t) = \varepsilon_{ii}$, in which Einstein's summation convention is used. Following the work of (Yoon and Allen, 1999; Seidel et al., 2005), the specific continuum damage evolution law in this study is assumed to be asymptotic and takes the form as below:

$$\dot{\alpha}(\mathbf{x}, t) = c(1 - \alpha(\mathbf{x}, t))^a \varepsilon_e(\mathbf{x}, t)^b$$
(7.5)

in which a, b, and c are material constants.

For the piezoresistive effect of the CNT-polymer nanocomposites, the dominant electrical tunneling effect among the CNTs is considered within the microscale. The electrical tunneling algorithm within the finite element domain has been discussed in detail in our previous work in (Ren and Seidel, 2013b). The tunneling resistivity within the critical tunneling distance is expressed as:

$$\rho_{\text{tunnel}} = \frac{h^2}{e^2 \sqrt{2m\lambda(\alpha)}} exp(\frac{4\pi d}{h} \sqrt{2m\lambda(\alpha)})$$
(7.6)

in which h is Planck's constant, d is the distance between adjacent CNTs, e is the electric charge, m is the mass of electron, and $\lambda(\alpha)$ is the height of barrier of the polymer matrix. It

159

is proposed that the height of barrier of the polymer matrix is linearly interpolated by the continuum damage parameter α , such that

$$\lambda(\alpha) = \lambda_{\rm o}(1-\alpha) + \lambda_{\rm void}\alpha \tag{7.7}$$

in which λ_{o} is the original height of barrier of the polymer matrix without damage, and λ_{void} is the height of barrier of the fully damaged void. The height of barrier of the polymer matrix is linearly transited from the one of the original polymer matrix to the one of the void. When $\alpha = 0$, there is no damage in the polymer matrix therefore $\lambda(0) = \lambda_{o}$, and when $\alpha = 1$, the polymer matrix is considered to be fully damaged voids such that $\lambda(1) = \lambda_{void}$. As observed in Fig. 7.1, when damage is developed from $\alpha = 0.0$ to $\alpha = 0.5$ to $\alpha = 1.0$, the electrical tunneling resistivity is shifted up by orders of magnitude from the original non-damaged polymer matrix to the completely damaged voids. Applying this algorithm to all polymer matrix elements can lead to clearly visible pattern of tunneling paths within the matrix for percolated volume percentages, and the tunneling paths are evolving not only with the change of relative distances of the CNTs, but also with damage. The continuum damage and piezoresistivity is one-way coupled, and the piezoresistive response of the material can become an indicator of the accumulation of continuum damage within the polymer matrix.



Figure 7.1: The semi-log plot of the electrical tunneling resistivity ρ_{tunnel} with increase of the CNT separation distance d, as the height of barrier λ is kept at 1.0 eV ($\alpha = 0.0$), 2.0 eV ($\alpha = 0.5$), and 3.0 eV ($\alpha = 1.0$) respectively.

7.2.2 The Multiscale Continuum Damage and Piezoresistivity Coupled Finite Element Model

Limited by CPU memory and speed, a single scale finite element analysis for problems with large degrees of freedom or large number of time steps is usually computational expensive and sometimes infeasible. In particular, for materials with numerous nonnegligible microscale inclusions, significantly varying material properties or governing fields, a multiscale analysis can be a wise choice. However, in the multiscale analysis different scales have to be able to effectively communicate with each other, in other words, the influence of one scale on another has to be taken into well account. In our model, the multiscale finite element analysis is conducted in two scales, and an in-house finite element code is developed. For the macroscale finite element analysis, the microscale information is concurrently taken through the course of the analysis, in a way such that at every element² of the macroscale mesh, the macroscale effective properties are obtained through homogenizations on the corresponding microscale RVEs; on the other hand, for the microscale finite element analysis, the macroscale information is applied concurrently to the corresponding microscale RVEs³. The detailed multiscale computational algorithm is illustrated in Fig. 7.2.

As seen in Fig. 7.2, for the multiscale continuum damage algorithm, firstly it is assumed that at a time step τ , for each macroscale element, the stiffness tensor for every element of the microscale RVE is known, which is denoted as $\mathbf{C}_{n_1,n_2}^{\tau}$. Microscale homogenization techniques (Hammerand et al., 2007) can then be applied to the microscale RVEs to obtain their effective properties, which are denoted as $\mathbf{C}_{n_1}^{\text{eff},\tau}$, and are used to represent the ones of the macroscale elements, i.e. $\tilde{\mathbf{C}}_{n_1}^{\tau} = \mathbf{C}_{n_1}^{\text{eff},\tau}$. Once the macroscale mechanical material properties are obtained from the microscale, the macroscale mechanical boundary value problem is solved based on the macroscale mesh, such that the strain tensor $\tilde{\boldsymbol{\varepsilon}}_{n_1}^{\tau}$ for every macroscale

 $^{^{2}}$ It is assumed that there is only one integration point per macroscale element, therefore only one microscale RVE is used to represent each macroscale element.

 $^{^{3}}$ We use the terminology 'microscale' to denote the lower length scale compared to the macroscale, although it is worth mentioning that in this study the RVE is small enough to be called 'nanoscale'.

Figure 7.2: The computational algorithm for implementing the multiscale finite element analysis. Note that the variables in '~' are macroscale variables, otherwise they are microscale variables. The macroscale element index $n_1 \in [1, n_M]$, in which n_M is the total number of macroscale elements, the microscale element index $n_2 \in [1, n_M]$, in which n_m is the total number of microscale elements, and the time step $\tau \in [0, \tau_T]$, in which τ_T is the total number of time steps.



element is obtained. The macroscale strain tensor $\tilde{\boldsymbol{\varepsilon}}_{n_1}^{\tau}$ is then applied back to the microscale RVE for each macroscale element as boundary conditions to get the local microscale material responses (for example, the strain tensor $\boldsymbol{\varepsilon}_{n_1,n_2}^{\tau}$ at every element of the microscale RVE can be obtained). Further, by applying Eq. (7.4), the current rate of damage parameter $\dot{\boldsymbol{\alpha}}_{n_1,n_2}^{\tau}$ and the predicted damage parameter $\boldsymbol{\alpha}_{n_1,n_2}^{\tau+1}$ at time step $\tau + 1$ for every microscale element of each macroscale element can be obtained. Having known the damage parameter $\boldsymbol{\alpha}_{n_1,n_2}^{\tau+1}$ at time step $\tau + 1$, by applying Eq. (7.1), the damaged microscale stiffness matrix $\mathbf{C}_{n_1,n_2}^{\tau+1}$ for every microscale element of each macroscale element of each macroscale element at time step $\tau + 1$ can therefore be obtained, and then the computations can go on to be conducted at the next time step.

For the multiscale piezoresistive algorithm, as seen in Fig. 7.2, with the macroscale strain tensor $\tilde{\varepsilon}_{n_1}^{\tau}$ applied as boundary conditions for each corresponding microscale RVE, the resistivities ρ_{n_1,n_2}^{τ} of the microscale elements may not only be changed by the change of relative distances of the CNT, but also be changed by continuum damage. Homogenization techniques (Ren and Seidel, 2013a) are then applied to the microscale RVEs to obtain their effective resistivities $\rho_{n_1}^{\text{eff},\tau}$, which are used to represent the effective resistivities of the macroscale elements, i.e. $\tilde{\rho}_{n_1}^{\tau}$. At last, with the resistivities $\tilde{\rho}_{n_1}^{\tau}$ of each macroscale element known, homogenization techniques are applied again at the macroscale to obtain the effective resistivities $\tilde{\rho}^{\text{eff},\tau}$ of the macroscale material as a whole at time step τ . It can be seen that the advantage of the multiscale model is that it gathers microscale information currently at different macroscale locations, and the mechanical-electrostatic inter-influence of different macroscale locations of the material can be well taken into account.

As seen in Eq. (7.4), the accumulated damage can have an influence on the rate of current damage parameter, therefore the material damage properties are history dependent. In order to keep 'memories' of the damage development, the Newmark method is used for both of the macroscale and the microscale finite element analysis. The Newmark method is an explicit time integration scheme mainly for solving dynamic problems, which is also highly accurate for solving quasi-static problems, and what is most important to us is that it has the advantage of keeping "memories".

7.3 Results and Discussion

For the single-walled CNTs considered herein, the outer radius is chosen to be 0.85nm, with the thickness of the annular region chosen to be 0.34nm (Schadler et al., 1998). Under small strain assumptions, the CNT annulus and Epoxy are taken to be isotropic linear elastic, with the Young's modulus and Poisson's ratio of 1100 GPa and 0.14, and 2.46 GPa and 0.3 respectively (Saito et al., 1998; Zhou et al., 2008). The tensile and compressive strengthes for Epoxy can vary in a large range (Prospector Materials Database), as such, the tensile and compressive strengthes of Epoxy are chosen to be 20 MPa and 60 MPa respectively, which are within its typical range. The material constants a, b, and c in Eq. 7.5 for the continuum damage evolution are chosen to be 0.6, 0.4, and 1.0 respectively. The initial isotropic resistivity within the CNT annulus is chosen to be $10^{-5} \Omega \cdot m$ (Ebbesen et al., 1996; Seidel and Lagoudas, 2009), and Epoxy is likewise isotropic with resistivity of $10^{14} \Omega \cdot m$ in the absence of electrical tunneling, which is within the typical range of values commonly reported for insulating polymers in experiments. Barrier height for Epoxy without damage is chosen to be $\lambda_o = 1.0 \text{ eV}$, which is within the typical range for Epoxy (0.5 eV - 2.5 eV) (Hu et al., 2012). It has been found that the height of barrier of void between several different metallics is between 3.0 - 4.0 eV (Ferrante and Smith, 1985), therefore in a similar manner we choose the height of barrier of void λ_{void} between CNTs to be 3.0 eV.

To simplify the problem, the focus is on the transverse performances of the CNT-polymer nanocomposites, such that the mechanical problems are formulated based on 2D plane-strain assumptions. For the macroscale and microscale problems, the linear triangular elements are used, therefore there is only one integration point per element and the strains and stresses are constantly distributed in the elements. In order to show how the multiscale model works, two numerical examples are demonstrated, with the first focused on the single microscale responses, as introduced in section 7.3.1, and the second focused on the macroscale and microscale coupled responses of the nanocomposites, as introduced in section 7.3.2.

7.3.1 The Microscale Continuum Damage and Piezoresistivity Coupled Response of the Nanocomposites

Consider a CNT-polymer nanocomposites in which there are 10%vol well-dispersed and aligned CNTs. To represent the material with such micro structure, we use the ideal microscale hexagonal RVE with 4 CNTs as seen in Fig. 7.3a, and in contrast the random microscale RVEs with 30 CNTs as seen in Fig. 7.3b and 7.3c. The three RVEs are intended

to compare with each other in terms of the coupled damage-piezoresistive effect to see the influence of CNT distributions and different damage evolution patterns on the piezoresistive response of the material. At zero strain, as there is no damage within the polymer matrix, the barrier height of the polymer matrix is constant at $\lambda_0 = 1.0$ eV, and due to different CNT distributions, the conductive paths are formed in different patterns for the three RVEs. For the hexagonal microscale RVE as seen in Fig. 7.3a, as the CNTs are hexagonally arranged to represent the well-dispersed and aligned CNTs, the conductive paths are correspondingly

to represent the well-dispersed and aligned CNTs, the conductive paths are correspondingly hexagonally well dispersed to electrically tunnel the adjacent CNTs. In contrast, for the random microscale RVEs as seen in Fig. 7.3b and 7.3c, as the CNTs are randomly dispersed in the transverse $X_1 - X_2$ plane, the conductive paths tend to become random. Stronger tunneling paths are formed among closer CNTs, and weaker tunneling paths are formed among farther away CNTs.



Figure 7.3: The zero-strain resistivity distributions of the three microscale RVEs for the polymer nanocomposites with 10%vol well-dispersed and aligned CNTs (Unit: $\Omega \cdot m$). a) The 10%vol microscale hexagonal RVE, b) The 10%vol microscale random RVE 1, c) The 10%vol microscale random RVE 2. Note that the barrier height of the polymer matrix without damage is chosen to be $\lambda_0 = 1.0 \text{ eV}$.

The plane-strain uniaxial tension tests under the macroscale strain field of ($\tilde{\varepsilon}_{22} = \tilde{\varepsilon}_0 =$



Figure 7.4: The Young's modulus (E) contours of the three 10%vol microscale RVEs at applied macroscale strain of $\tilde{\varepsilon}_0 = 0.50\%$ and $\tilde{\varepsilon}_0 = 0.85\%$ respectively (Unit: Pa). a1) The 10%vol hexagonal RVE at $\tilde{\varepsilon}_0 = 0.50\%$, a2) The 10%vol hexagonal RVE at $\tilde{\varepsilon}_0 = 0.85\%$, b1) The 10%vol random RVE 1 at $\tilde{\varepsilon}_0 = 0.50\%$, b2) The 10%vol random RVE 1 at $\tilde{\varepsilon}_0 = 0.85\%$, c1) The 10%vol random RVE 2 at $\tilde{\varepsilon}_0 = 0.50\%$, c2) The 10%vol random RVE 2 at $\tilde{\varepsilon}_0 = 0.85\%$.

0% - 0.85%, and $\tilde{\varepsilon}_{11} = -\nu'_{21}\tilde{\varepsilon}_0$) are applied to the three microscale RVEs⁴. The tests are intended to cause progressive continuum damage within the polymer matrix, and the coupled damage and piezoresistive effect is to be studied. The Young's modulus contours of the three RVEs at applied macroscale strain of $\tilde{\varepsilon}_0 = 0.50\%$ are shown in Fig. 7.4a1, 7.4b1, and 7.4c1 respectively. It can be observed that damage has accumulated in multiple places within the RVEs by satisfying the Christensen's failure criterion. For the hexagonal RVE, as the CNTs are ideally hexagonally dispersed, the continuum damage is the same for all of

⁴As in Ref. (Ren and Seidel, 2013a), ν'_{21} is the effective Poisson's ratio under plane-strain uniaxial tension test, and is obtained at zero strain without damage.

the CNTs, and for the two random RVEs, as the CNTs are randomly dispersed within the plane, the continuum damage can be coalesced between adjacent CNTs. Correspondingly, the resistivity contours of the three RVEs at applied macroscale strain of $\tilde{\varepsilon}_0 = 0.50\%$ are shown in Fig. 7.5a1, 7.5b1, and 7.5c1 respectively. It is observed in the RVEs that the resistivities are higher at the damaged places, which affect but has not blocked the conductive paths. The macroscale strains of the three RVEs are continued to be loaded at $\tilde{\varepsilon}_0 = 0.85\%$, with the Young's modulus contours shown in Fig. 7.4a2, 7.4b2, and 7.4c2 respectively. It is observed that compared to the contours at $\tilde{\varepsilon}_0 = 0.50\%$, the damage has further developed and coalesced with each other in most of the places within the RVEs. As a consequence, as observed in Fig. 7.5a2, 7.5b2, and 7.5c2, most of the conductive paths are influenced and

some of them are entirely blocked.

To further study the correlation between damage and piezoresistivity within the nanocomposites, the responses of the volume averaged stress σ_{22}^{avg} and the effective resistivity ρ_{22}^{eff} of the three RVEs with the applied boundary strain $\tilde{\varepsilon}_0$ from 0.0% to 0.85% are shown in Fig. 7.6. It is of interest to see that damages within the RVEs are not reflective on the stress curves until the applied boundary strain is at $\tilde{\varepsilon}_0 = 0.50\%$. In contrast, the effective resistivity curves are very sensitive to damage. Once there is damage within the polymer matrix, the effective resistivity curves can be immediately deviated from the ones without damage and upswing by orders of magnitude when there is more damage developed. This is because the average stress is the material's average response therefore it can not reflect local damage behaviors until the local damages have accumulated enough to influence the overall average response. In contrast, the piezoresistive response is reflective of the disturbance of conductive paths that electrically percolate the material, therefore once there is change in the conductive paths, it can be immediately reflected in the change of effective resistivity of the material.

It is also of interest to notice that the stress curves of the three RVEs are nearly the same. At $\tilde{\varepsilon}_0 = 0.85\%$, the average stress are 1.43×10^7 Pa, 1.48×10^7 Pa, and 1.46×10^7 Pa respectively for the three RVEs. In contrast, the resistivity curves of the three RVEs can have a large



Figure 7.5: The resistivity (ρ) contours of the three 10%vol microscale RVEs at applied macroscale strain of $\tilde{\varepsilon}_0 = 0.50\%$ and $\tilde{\varepsilon}_0 = 0.85\%$ respectively (Unit: Pa). a1) The 10%vol hexagonal RVE at $\tilde{\varepsilon}_0 = 0.50\%$, a2) The 10%vol hexagonal RVE at $\tilde{\varepsilon}_0 = 0.85\%$, b1) The 10%vol random RVE 1 at $\tilde{\varepsilon}_0 = 0.50\%$, b2) The 10%vol random RVE 1 at $\tilde{\varepsilon}_0 = 0.85\%$, c1) The 10%vol random RVE 2 at $\tilde{\varepsilon}_0 = 0.50\%$, c2) The 10%vol random RVE 2 at $\tilde{\varepsilon}_0 = 0.85\%$.

difference in magnitudes. From $\tilde{\varepsilon}_0 = 0.0\%$ to $\tilde{\varepsilon}_0 = 0.85\%$, the effective resistivity of the hexagonal RVE is increased from $1.24 \times 10^{11} \ \Omega \cdot m$ to $1.55 \times 10^{16} \ \Omega \cdot m$, and by comparison the effective resistivities of the two random RVEs are increased from $1.53 \times 10^8 \ \Omega \cdot m$ to $1.02 \times 10^{13} \ \Omega \cdot m$ and from $8.71 \times 10^{10} \ \Omega \cdot m$ to $2.87 \times 10^{17} \ \Omega \cdot m$ respectively. This is because unlike the mechanical response which is linear elastic, the piezoresistive response is governed by the exponential governing laws as in Eq. (7.6), such that dispersion of the CNTs can matter more in terms of piezoresistive response. For example, as seen in Fig. 7.5b1 and 7.5c1, by comparing the two random RVEs at $\tilde{\varepsilon}_0 = 0.0\%$, it can be seen that due to nonhomogeneous dispersion of the CNTs, the conductive paths are generally stronger in RVE 1 than in RVE 2 in X₂ direction, causing its effective resistivity to be 2 orders lower than RVE 2. With the macroscale strains applied at $\tilde{\varepsilon}_0 = 0.85\%$, as seen in Fig. 7.5b2 and 7.5c2, although due to damage the conductive paths in RVE 1 are severely disturbed, compared to RVE 2, they are still able to electrically percolate the material, therefore the effective resistivity of RVE 1 at $\tilde{\varepsilon}_0 = 0.85\%$ is 4 orders lower than the one of RVE 2. Therefore it can be seen that the distribution of CNTs is an important factor as it can influence both of the local damage and the electrical tunneling paths, and the coupled effect of which are important for the overall piezoresistivity of the material.

So far, we have studied the coupled continuum damage and piezoresistive response in the microscale, and good correlation is found between them. The microscale piezoresistive response of the CNT-polymer nanocomposites is found to be able to capture the local damage behavior and immediately reflect the damage events on the piezoresistive curves. In section 7.3.2, by using the concurrent multiscale model, we will study how the microscale damage and piezoresistive events have an inter influence on the macroscale material behaviors.

7.3.2 The Multiscale Continuum Damage and Piezoresistivity Coupled Response of the Nanocomposites

Consider a macroscale square specimen $(1 \text{ cm} \times 1 \text{ cm})$ has a thick depth in \tilde{X}_3 direction, and has a hole ($\tilde{r} = 0.5 \text{ cm}$) at the center, as seen in Fig. 7.7. The specimen is made of polymer nanocomposites with 10%vol well-dispersed and aligned CNTs in \tilde{X}_3 direction. Plane-strain uniaxial tension test is applied to the specimen with a macroscale boundary strain $\tilde{\varepsilon}_{22}^{\text{B}}$ of 0.0% to 0.5%, and our goal is to obtain its coupled damage and piezoresistive response. Due to a seven orders difference of the dimensions of the macroscale specimen and the CNT, it would be tremendously expensive in terms of computation and unrealistic by using a single scale simulation. As such, a concurrent multiscale simulation as proposed in section 7.2.2 is used. The macroscale specimen is meshed by 707 elements, and for every integration point of the specimen, there is a corresponding 10%vol microscale RVE as shown in Fig. 7.3a used





Figure 7.6: The coupled damage-piezoresistive response of the three 10%vol microscale RVEs as the applied macroscale strain $\tilde{\varepsilon}_0$ is from 0% to 0.85% (Stress unit: Pa; Resistivity unit: $\Omega \cdot m$). a) The change of average stress σ_{22}^{avg} and effective resistivity ρ_{22}^{eff} for the 10%vol hexagonal RVE, b) The change of average stress σ_{22}^{avg} and effective resistivity ρ_{22}^{eff} for the 10%vol RVE 1, c) The change of average stress σ_{22}^{avg} and effective resistivity ρ_{22}^{eff} for the 10%vol RVE 2. Note that the resistivity curves are in semi-log scale.

to represent the well-dispersed and aligned CNTs in the microscale.

Under the macroscale plane-strain uniaxial tension test, the multiscale coupled damage and piezoresistive responses of the specimen are obtained and we chose to use the elements 130, 132, and 460 as shown in Fig. 7.7 to demonstrate the microscale responses at these three distinct macroscale locations. As seen in Fig. 7.8a1 and 7.8a2, for element 460 at $\varepsilon_{22}^{\rm B} = 0.5\%$, as there is no continuum damage within the polymer matrix, the conductive paths are intact by damage. In contrast, as seen in Fig. 7.8b1 and 7.8b2, for element 130 at $\varepsilon_{22}^{\rm B} = 0.5\%$,



Figure 7.7: Illustration of the macroscale finite element model under plane-strain uniaxial tension test of $\tilde{\varepsilon}_{22}^{\rm B} = 0.0\% - 0.5\%$. Note that 707 elements are used for the mesh. Note that the origin of the macroscale coordinate system is at the center of the hole.

as the blue regions are the damaged polymer matrix regions, the conductive paths of these regions are blocked. However, the material can still be electrically percolated in both X_1 and X_2 directions. Further for element 132 as seen in Fig. 7.8c1 and 7.8c2, as the polymer matrix is mostly damaged, the conductive paths are entirely blocked.

The effective stiffness tensor component C_{22}^{eff} and the effective resistivity ρ_{22}^{eff} of all the elements can be obtained through energy equivalence methods and are substituted into the macroscale such that $\tilde{C}_{22} = C_{22}^{\text{eff}}$ and $\tilde{\rho}_{22} = \rho_{22}^{\text{eff}}$. For $\varepsilon_{22}^{\text{B}} = 0.0\% - 0.5\%$, the change of \tilde{C}_{22} and $\tilde{\rho}_{22}$ for elements 130, 132, and 460 are shown in Fig. 7.9(a) and 7.9(b). It can be observed that the more damaged elements have a lower \tilde{C}_{22} , and at the same time a higher $\tilde{\rho}_{22}$ due to different degrees of disturbance of the conductive paths.

Through concurrent macroscale and the microscale computations, the contours of the effective stiffness tensor component \tilde{C}_{22} of the macroscale specimen at $\tilde{\varepsilon}_{22}^{\rm B} = 0.25\%$ and $\tilde{\varepsilon}_{22}^{\rm B} = 0.5\%$ are shown in Fig. 7.10a1 and Fig. 7.10a2 respectively. It can be observed that at $\tilde{\varepsilon}_{22}^{\rm B} = 0.25\%$, there is initial damage accumulated at coordinates (0.5,0) and (-0.5,0) on the hole, causing the stiffness \tilde{C}_{22} to be reduced. Further at $\tilde{\varepsilon}_{22}^{\rm B} = 0.50\%$, the damage is developed to more



Figure 7.8: The piezoresistive responses of the microscale RVEs at elements 130, 132, and 460 respectively of the specimen at $\varepsilon_{22}^{\rm B} = 0.5\%$. a1) Contour of Young's modulus of element 460 at $\varepsilon_{22}^{\rm B} = 0.5\%$. b1) Contour of Young's modulus of element 130 at $\varepsilon_{22}^{\rm B} = 0.5\%$. c1) Contour of Young's modulus of element 132 at $\varepsilon_{22}^{\rm B} = 0.5\%$. a2) Contour of resistivity of element 460 at $\varepsilon_{22}^{\rm B} = 0.5\%$. b2) Contour of resistivity of element 130 at $\varepsilon_{22}^{\rm B} = 0.5\%$. c2) Contour of resistivity of element 132 at $\varepsilon_{22}^{\rm B} = 0.5\%$.

regions within the specimen, with the less damaged regions look like a 'sandglass'. Similar contours can be observed in the von Mises strain distributions within the specimen, as shown in Fig. 7.10b1 and Fig. 7.10b2. This is because the more damaged regions have lower stiffness such that the strains are more easily concentrated at these regions. The contours of effective conductivity component $\tilde{\kappa}_{22}$ ($\tilde{\rho}_{22}^{-1}$) of the specimen at $\tilde{\varepsilon}_{22}^{\rm B} = 0.25\%$ and $\tilde{\varepsilon}_{22}^{\rm B} = 0.5\%$ are shown in Fig. 7.10c1 and Fig. 7.10c2 respectively. By comparing to the contours at Fig. 7.10a1 and Fig. 7.10a2, it can be clearly observed that the conductivity contours can reflect the damage regions very well, i.e. the more damaged regions have lower conductivities. Therefore, it can



Figure 7.9: The material responses of the macroscale specimen at elements 130, 132, and 460 respectively. a) The change of macroscale stiffness tensor component \tilde{C}_{22} with the change of macroscale boundary strain $\tilde{\varepsilon}_{22}^{\text{B}}$ for elements 130, 132, and 460 respectively of the specimen. b) The change of macroscale resistivity component $\tilde{\rho}_{22}$ with the change of macroscale boundary strain $\tilde{\varepsilon}_{22}^{\text{B}}$ for elements 130, 132, and 460 respectively of the specimen.

be seen from the contours that there is a good correlation between the continuum damage and piezoresistivity in the macroscale specimen made of CNT-polymer nanocomposites.

The volume averaged stress component $\tilde{\sigma}_{22}^{\text{avg}}$ and the effective resistivity component $\tilde{\rho}_{22}^{\text{eff}}$ for the macroscale specimen under uniaxial tensile tension test are plotted in Fig. 7.11. It is again found that the stress response at the macroscale is not sensitive to the microscale damages until they are accumulated enough (at $\tilde{\varepsilon}_{22}^{\text{B}} = \sim 0.32\%$) to influence the overall stress response. On the other hand, the piezoresistive response of the macroscale specimen is very sensitive to the underling microscale damage, and can reflect damages immediately by upswinging the resistivity curve compared to the one without damage. However, compared to the microscale piezoresistive responses that can increase by orders of magnitude, the macroscale resistivity is increased within the same order from $1.87 \times 10^{11} \ \Omega \cdot m$ to 4.45×10^{11} $\Omega \cdot m$. This is because for the macroscale specimen, although the more damaged regions can have orders of magnitude higher resistivity, the macroscale electrical flux can be still be electrically conducted by the less damaged regions such that the conducting paths are not entirely blocked in \tilde{X}_2 direction. Therefore we can say that the overall piezoresistive response



Figure 7.10: The contours of the stiffness tensor component \tilde{C}_{22} , the von Mises strain $\tilde{\varepsilon}_{v}$, and the conductivity $\tilde{\kappa}_{22}$ of the macroscale specimen at applied boundary strain $\tilde{\varepsilon}_{22}^{B}$ of 0.25% and 0.50% respectively. a1) Contour of \tilde{C}_{22} at $\tilde{\varepsilon}_{22}^{B} = 0.25\%$, b1) Contour of $\tilde{\varepsilon}_{v}$ at $\tilde{\varepsilon}_{22}^{B} = 0.25\%$, c1) Contour of $\tilde{\kappa}_{22}$ at $\tilde{\varepsilon}_{22}^{B} = 0.25\%$, a2) Contour of \tilde{C}_{22} at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$, b2) Contour of $\tilde{\varepsilon}_{v}$ at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$, c2) Contour of $\tilde{\kappa}_{22}$ at $\tilde{\varepsilon}_{22}^{B} = 0.50\%$. Note that the conductivity $\tilde{\kappa}_{22}$ is the inverse of resistivity $\tilde{\rho}_{22}$.

of the specimen is alleviated by the less damaged regions.

7.4 Conclusions

A computational concurrent multiscale piezoresistive modeling work is developed to study the coupled continuum damage and piezoresistive effect of CNT-polymer nanocomposites. It is found that the piezoresistive response of the nanocomposites is very sensitive to damage events at both of the microscale and the macroscale, and can detect small damage events before large scale damage events happen. This coupled damage-piezoresistive response of the



Figure 7.11: The coupled damage-piezoresistive response of the macroscale specimen as the applied macroscale boundary strain $\tilde{\varepsilon}_{22}^{\text{B}}$ is from 0% to 0.50% (Stress unit: Pa; Resistivity unit: $\Omega \cdot \text{m}$).

CNT-polymer nanocomposites is also found in various experimental testings in the literature, for example in the work of (Gao et al., 2009a,b; Saafi, 2009; Kim et al., 2010; Cardoso et al., 2012; Heeder et al., 2012). By studying the mechanism of the coupling between continuum damage and piezoresistivity, this work gives theoretical and modeling support for the CNTpolymer nanocomposites to be used in SHM applications.

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Appendix A

Periodic boundary conditions for the plane-strain uniaxial tension test

For the macroscale effective homogeneous material, the constitutive relationship can be denoted as

$$\left\{ \begin{array}{c} \tilde{\varepsilon}_{11} \\ \tilde{\varepsilon}_{22} \\ \tilde{\varepsilon}_{33} \\ \tilde{\varepsilon}_{33} \\ 2\tilde{\varepsilon}_{23} \\ 2\tilde{\varepsilon}_{13} \\ 2\tilde{\varepsilon}_{12} \end{array} \right\} = \left[\begin{array}{c} \frac{1}{\mathrm{E}_{11}^{\mathrm{Eff}}} & -\frac{\nu_{21}^{\mathrm{Eff}}}{\mathrm{E}_{22}^{\mathrm{Eff}}} & 0 & 0 & 0 \\ -\frac{\nu_{12}^{\mathrm{Eff}}}{\mathrm{E}_{22}^{\mathrm{Eff}}} & \frac{1}{\mathrm{E}_{22}^{\mathrm{Eff}}} & -\frac{\nu_{33}^{\mathrm{Eff}}}{\mathrm{E}_{33}^{\mathrm{Eff}}} & 0 & 0 & 0 \\ -\frac{\nu_{13}^{\mathrm{Eff}}}{\mathrm{E}_{11}^{\mathrm{Eff}}} & -\frac{\nu_{23}^{\mathrm{Eff}}}{\mathrm{E}_{22}^{\mathrm{Eff}}} & 0 & 0 & 0 \\ -\frac{\nu_{13}^{\mathrm{Eff}}}{\mathrm{E}_{11}^{\mathrm{Eff}}} & -\frac{\nu_{23}^{\mathrm{Eff}}}{\mathrm{E}_{22}^{\mathrm{Eff}}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{\mathrm{G}_{23}^{\mathrm{Eff}}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{\mathrm{G}_{13}^{\mathrm{Eff}}} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{\mathrm{G}_{13}^{\mathrm{Eff}}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{\mathrm{G}_{13}^{\mathrm{Eff}}} \end{array} \right] \left\{ \begin{array}{c} \tilde{\sigma}_{11} \\ \tilde{\sigma}_{22} \\ \tilde{\sigma}_{33} \\ \tilde{\sigma}_{23} \\ \tilde{\sigma}_{13} \\ \tilde{\sigma}_{12} \end{array} \right\}$$
(A.1)

in which under in-plane strain assumption, $\tilde{\varepsilon}_{33} = \tilde{\varepsilon}_{23} = \tilde{\varepsilon}_{13} = 0$. For the plane-strain uniaxial tension test with ε_0 applied in 2 direction,

$$\tilde{\varepsilon}_{22} = \varepsilon_0$$
 (A.2a)

$$\tilde{\sigma}_{11} = 0 \tag{A.2b}$$

Therefore,

$$\tilde{\varepsilon}_{11} = -\frac{\nu_{21}^{\text{Eff}}}{E_{22}^{\text{Eff}}} \tilde{\sigma}_{22} - \frac{\nu_{31}^{\text{Eff}}}{E_{33}^{\text{Eff}}} \tilde{\sigma}_{33}$$
(A.3a)

$$\varepsilon_0 = \frac{1}{E_{22}^{\text{Eff}}} \tilde{\sigma}_{22} - \frac{\nu_{32}^{\text{Eff}}}{E_{33}^{\text{Eff}}} \tilde{\sigma}_{33}$$
(A.3b)

$$0 = -\frac{\nu_{23}^{\text{Eff}}}{E_{22}^{\text{Eff}}} \tilde{\sigma}_{22} + \frac{1}{E_{33}^{\text{Eff}}} \tilde{\sigma}_{33}$$
(A.3c)

Substitute (A.3b) and (A.3c) into (A.3a),

$$\tilde{\varepsilon}_{11} = -\frac{\nu_{21}^{\text{Eff}} + \nu_{31}^{\text{Eff}}\nu_{23}^{\text{Eff}}}{1 - \nu_{32}^{\text{Eff}}\nu_{23}^{\text{Eff}}}\varepsilon_0 = -\nu_{21}'\varepsilon_0 \tag{A.4}$$

The non-zero strain components $\tilde{\varepsilon}_{11}$ and $\tilde{\varepsilon}_{22}$ can then be applied as periodic boundary conditions to the hexagonal nanoscale RVE of Fig. 3.2a, in which the effective Poisson's ratios can be obtained by using either computational micromechanics method (Hammerand et al., 2007) or by using composite cylinder method (Seidel and Lagoudas, 2006).

Appendix B

Derivations of the effective gauge factors for the plane-strain tension tests

To obtain the effective gauge factors for the plane-strain tension tests, Eq. (2.38) is used. As derived in A, for the macroscale plane-strain uniaxial tension test,

$$\tilde{\varepsilon}_{11} = -\frac{\nu_{21}^{\text{Eff}} + \nu_{31}^{\text{Eff}} \nu_{23}^{\text{Eff}}}{1 - \nu_{32}^{\text{Eff}} \nu_{23}^{\text{Eff}}} \varepsilon_0$$
(B.1a)

$$\tilde{\varepsilon}_{22} = \varepsilon_0$$
 (B.1b)

$$\tilde{\varepsilon}_{33} = 0$$
 (B.1c)

Therefore,

$$L^{f} = L^{0}(1 + \tilde{\varepsilon}_{22})$$
$$= L^{0}(1 + \varepsilon_{0})$$
(B.2a)

$$A^{f} = A^{0}(1 + \tilde{\varepsilon}_{11})(1 + \tilde{\varepsilon}_{33})$$

= $A^{0}(1 - \frac{\nu_{21}^{\text{Eff}} + \nu_{31}^{\text{Eff}}\nu_{23}^{\text{Eff}}}{1 - \nu_{21}^{\text{Eff}}\nu_{23}^{\text{Eff}}}\varepsilon_{0})$ (B.2b)

$$\rho^{0} = \rho_{22}^{\text{Eff}}(0) \tag{B.2c}$$

$$\rho^{\rm f} = \rho^{\rm Eff}_{22}(\varepsilon_0) \tag{B.2d}$$

Substitute Eq.s (B.2a) to (B.2d) into Eq. (2.38),

$$G^{\text{Eff}} = \frac{1}{\varepsilon_0} \left(\frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} \frac{1 + \varepsilon_0}{1 - \frac{(\nu_{21}^{\text{Eff}} + \nu_{31}^{\text{Eff}} \nu_{23}^{\text{Eff}})\varepsilon_0}{1 - \nu_{32}^{\text{Eff}} \nu_{23}^{\text{Eff}}} - 1 \right)$$
(B.3)

Similarly, for the macroscale plane-strain biaxial tension test,

$$\tilde{\varepsilon}_{11} = \varepsilon_0$$
 (B.4a)

$$\tilde{\varepsilon}_{22} = \varepsilon_0$$
 (B.4b)

$$\tilde{\varepsilon}_{33} = 0$$
 (B.4c)

Therefore,

$$L^{f} = L^{0}(1 + \tilde{\varepsilon}_{22})$$
$$= L^{0}(1 + \varepsilon_{0})$$
(B.5a)

$$A^{f} = A^{0}(1 + \tilde{\varepsilon}_{11})(1 + \tilde{\varepsilon}_{33})$$
$$= A^{0}(1 + \varepsilon_{0})$$
(B.5b)

$$\rho^0 = \rho_{22}^{\text{Eff}}(0) \tag{B.5c}$$

$$\rho^{\rm f} = \rho^{\rm Eff}_{22}(\varepsilon_0) \tag{B.5d}$$

Substitute Eq.s (B.5a) to (B.5d) into Eq. (2.38),

$$\mathbf{G}^{\text{Eff}} = \frac{1}{\varepsilon_0} \left(\frac{\rho_{22}^{\text{Eff}}(\varepsilon_0)}{\rho_{22}^{\text{Eff}}(0)} - 1 \right) \tag{B.6}$$

Appendix C

Geometry correspondence between axial and transverse RVEs

For the axisymmetric nanoscale RVE as seen in Fig. 3.2b, the volume fraction of CNT is

$$V_{f} = \frac{L_{CNT} R_{out}^{2} \pi}{L \cdot R^{2} \pi}$$
(C.1)

in which,

$$L_{\rm CNT} = AR(2R_{\rm out}) \tag{C.2a}$$

$$L = L_{CNT} + 2L_s \qquad (C.2b)$$

 L_s is the separation distance between the ends of the CNT to the boundaries of the axisymmetric RVE. Substitute Eq.s (C.2a) and (C.2b) into Eq. (C.1),

$$V_{f} = \frac{AR \cdot R_{out}^{3}}{(AR \cdot R_{out} + L_{s})R^{2}}$$
(C.3)

As

$$L_s \ge 0 \text{ and } R \ge R_{out}$$
 (C.4)

substitute $R = R_{out}$ into Eq. (C.3), one can obtain

$$0 \le L_s \le AR \cdot R_{out}(\frac{1}{V_f} - 1)$$
(C.5)

Choose $L_s = L_s(AR = 1)$ as a constant parameter for the RVEs with higher aspect ratio CNTs, and it can be seen that as $AR \rightarrow \infty$,

$$\frac{L_{CNT}}{L} = \frac{AR \cdot R_{CNT}}{AR \cdot R_{CNT} + L_s(AR = 1)} \to 1$$
(C.6a)

and

$$R \rightarrow \frac{R_{out}}{\sqrt{V_f}}$$
 (C.6b)

which is the limit case for which the transverse hexagonal RVE is a good approximation.

Appendix D

Verification on the finite element piezoresistive modeling work

The linear elastic and electrostatic (without electron hopping) modeling works are first verified by comparing with the ones obtained from ABAQUS. For the linear elastic problem, a plane-strain biaxial tension test ($\varepsilon_0 = 1\%$) is applied to the nanoscale hexagonal RVE with 10%vol CNTs. The contours of ε_{11} and σ_{11} as obtained from my modeling work and ABAQUS are shown side by side in Fig. D.1. It can be seen that the contours match very well. By comparing ε_{11} , ε_{22} , ε_{12} , σ_{11} , σ_{22} , and σ_{12} between my modeling results and the ones from ABAQUS at the integration points, it is found that the maximum relative differences are 0.013%, 0.023%, 0.0098%, 0.013%, 0.0024%, 0.040% respectively for all the elements (N_E=1 to 25012).

For the electrostatic problem without electron hopping effect and for the same nanoscale RVE, a relative potential difference of $\Delta \Phi = 10.239$ V is applied between the top edge and the bottom edge. The contours of E_i and EPG_i as obtained from my modeling work and from ABAQUS are shown side by side in Fig. D.2. Note that the contours are inverse as $E_i = -\frac{\partial \Phi}{\partial x_i}$, and EPG_i = $\frac{\partial \Phi}{\partial x_i}$. By comparing the electric fields E_i between my modeling results and the ones from ABAQUS at the integration points, it is found that the maximum relative



Figure D.1: Comparison of my modeling work and the ones as obtained from ABAQUS for the linear elastic problem. a) Contour of ε_{11} from my modeling work, b) Contour of ε_{11} from ABAQUS, c) Contour of σ_{11} from my modeling work, d) Contour of σ_{11} from ABAQUS. Note that the mesh contains 12803 nodes and 25012 elements.

differences are 1.0% and 0.026% respectively for all the elements ($N_E=1$ to 25012). Therefore by comparing with ABAQUS, it is verified that my linear elastic and electrostatic (without hopping) modeling works are correct.



Figure D.2: Comparison of my modeling work and the ones as obtained from ABAQUS for the electrostatic problem without electron hopping. a) Contour of E_1 from my modeling work, b) Contour of EPG₁ from ABAQUS, c) Contour of E_2 from my modeling work, d) Contour of EPG₂ from ABAQUS. Note that $E_i = -\frac{\partial \Phi}{\partial x_i}$ and $EPG_i = \frac{\partial \Phi}{\partial x_i}$.

For the piezoresistive modeling work, i.e. in which the mechanical and electrostatic responses are coupled, the distribution of resistivity component ρ_{22} of the hexagonal nanoscale RVE with 10%vol CNTs under plane-strain biaxial tension test of $\varepsilon_0 = 1.0\%$ is shown in Fig. D.3. It is checked that the resistivities of all the polymer matrix elements exactly follow the governing equation curve of $\lambda = 0.5$ eV in Fig. 3.3, and the resistivities of the CNTs exactly follow the piezoresistive constitutive Eq. 2.31. Therefore it is verified that the piezoresistive modeling work is correct.



Figure D.3: The contour of resistivity component ρ_{22} of the hexagonal nanoscale RVE with 10%vol CNTs under plane-strain biaxial tension test of $\varepsilon_0 = 1.0\%$ ($\lambda = 0.5$ eV).