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Microstructural-Based Modeling of Electrical Percolation In Polymer Nanocomposites

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MICROSTRUCTURAL-BASED MODELING OF ELECTRICAL PERCOLATION IN
POLYMER NANOCOMPOSITES

by

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Dedication

To my parents,

Yellepeddi Veerabhadra Sarma and Yellepeddi Annapurna,

for being my constant source of inspiration and always believing in me.

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ABSTRACT

Polymer nanocomposites (PNCs) represent a radical alternative to conventional filled polymers or polymer blends. In contrast to conventional composites, where the included phase is on the order of micrometers, PNCs are defined as those that have discrete constituents on the order of a few hundred nanometers. The value of PNCs is not solely based on tailoring mechanical properties, as in traditional composite design and manufacture, but rather on the potential for the design and optimization of multi-functional properties. There is major interest in these polymeric materials embedded with a conductive nanoscale filler. This is due to the possibility of designing a composite that retains the easy processing of plastics but can take advantage of a conductive nanoscale phase; providing electrical conductivity in additional to structural reinforcement.

The challenge to modeling multi-functional properties of PNCs is that, traditionally, different models have been applied to model different properties. Mechanical properties are most often modeled using mean-field models from micromechanics; properties depend on the microstructural arrangement of the included phase, phase properties and volume fraction. Electrical conductivity has primarily been modeled using percolation theory and power-law models; properties depend on theoretical or simulation based estimates of a percolation threshold, phase properties and volume fraction. However, models of both properties should ideally be built on specific microstructural descriptions as well as include a probabilistic framework to capture percolation effects.

In this work a modeling framework, developed for predicting composite mechan-

ical properties, is investigated for its applicability in modeling effective electrical composite properties. The basis for using a micromechanics approach for predictions of conductivity is presented as well as how the model is adapted to model conductivity. A comparison of the adapted and original micromechanics approach is presented for deterministic microstructures. The modeling framework is subsequently used to predict the effective electrical conductivity of a model PNC. Using the micromechanical parameters of interface thickness and properties, the model can be adjusted to correspond with observed experimental and is useful in suggesting underlying mechanisms.

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Chapter 1

Introduction

The primary reason for the development of composite materials is the goal of combining the properties of multiple constituent materials in a very advantageous manner, tailoring properties to application. Polymer nanocomposites (PNCs) represent a radical alternative to conventional filled polymers or polymer blends. In contrast to conventional composites, where the included phase is on the order of micrometers, PNCs are exemplified by discrete constituents on the order of a few hundred nanometers. The value of PNCs is not solely based on tailoring mechanical properties, as in traditional composite design and manufacture, but rather on the potential for the design and optimization of multi-functional properties. An example is the interest in the rapidly growing field of flexible and stretchable electronics. The primary interest in polymeric materials embedded with a conductive nanoscale filler is based on the potential to design a composite that retains the easy processing of plastics but takes advantage of a conductive nanoscale phase. The composite is electrically conductive and has superior structural properties to the neat polymer.

The challenge to modeling multi-functional properties of PNCs is that, traditionally, different models have been applied to model different properties. Mechanical properties are most often modeled using mean-field models from micromechanics; properties depend on the microstructural arrangement of the included phase, phase properties and volume fraction. Electrical conductivity in composites has primarily been modeled using percolation theory and power-law models; properties depend on theoretical or simulation based estimates of a percolation threshold, phase properties

and volume fraction. However, models of both properties, should be built on specific a microstructural descriptions as well as include a probabilistic framework to capture percolation effects.

In this work a modeling framework, developed for mechanical properties, is investigated for use modeling effective electrical composite properties. This approach combines the two model types, deterministic estimates of the physical property and probabilistic descriptions of random microstructural arrangement, into a single modeling approach. The effect of microstructure and the effect of scale are reflected in the model by including the effects of an interfacial layer between the included phase and the polymeric matrix. The model approach is validated though a comparison to experimental data from the literature.

Chapter 2 provides a brief review of the literature discussing the interest in polymer nanocomposites, some current experimental and modeling efforts and previous work that has used micromechanics as the base for modeling electrical conductivity. Chapter 3 traces the historical path of models capturing the effective electrical conductivity of composites from early effective medium models through classic power-law percolation models and into general conductive laws that combine elements of both. Chapter 4 discusses the applicability of using classic micromechanics formulations to model effective conductivity and presents an overview of the computational micromechanics model used in this work. Chapter 5 outlines the model adaptations and their observable distinguishing effects on modeling mechanical or electrical properties. Chapter 6 describes a model material system and gives an overview of the experimental work on which the modeling is based. Chapter 7 presents the results of modeling composite electrical conductivity for a model material system and compares the results to experimental work. Chapter 8 provides a summary of the results and suggestions for future work.

Chapter 2

Literature Review

This chapter provides a review of some of the literature on multifunctional polymer nanocomposites, PNCs; applications and current modeling and experimental work.

2.1 Applications of Polymer Nanocomposites

Polymer nanocomposites have a wide range of potential application, largely from the the growing field of flexible and stretchable electronics, but other advantageous properties can also be achieved. A recent article in *Nanotechnology* [1] reviewed the possible applications for nano-structured materials as engineered materials.

Flexible electronic devices can be bent, rolled and stretched into arbitrary shapes, which can increase the applications of electronic devices in the areas of computation, communications, displays, sensing and energy harvesting. Mechanically flexible devices are capable of bending around curved surfaces and have potential applications in roll-able photovoltaics due to their easy installation [2] and displays [3], as well as for electronic skins for robotics and prosthetics [4].

In addition to bending and twisting, certain applications require to be stretched without delamination, separation or fracture of the electrical components. In the future, the concept of integrated electronics on stretch-tolerant polymer nanocomposites may be expanded to enable multi-functional artificial electronic-skins through the addition of active electronic and sensor device components.

The ability to attach to arbitrary surfaces without the need of magnetic or mechanical adhesives is another potential asset of PNCs. At the macroscale level, zippers

and velcro are used, but at the nanoscale, polymer nanocomposites can act as adhesives that attach through van der Waals interactions. The two main advantages of this are the ability to shrink down the size of binding sites and the ability to maintain adhesion strength after multiple attachment and detachment cycles.

Electronic devices which have self-cleaning surfaces can be made water proof and dust free. For example, self-cleaning surfaces in solar panels can increase light conversion efficiency by reducing the dust build-up which could potentially block the sunlight [5]. Also, self-cleaning surfaces with minimal fingerprint residue are desirable for touch pads.

Anti-reflective surfaces find their applications in displays, photovoltaics and photodetectors. Anti-reflective surfaces can be fabricated by the formation of tapered three dimensional nanostructures on the target substrates.

Finally, nanocomposites may help in the design of stimuli responsive devices. These are structures which can reversibly change shape, color, other physical/chemical properties in response to external stimuli such as mechanical stress, light, heat, moisture or changes in pH. These programmable materials have applications in microbiotics, artificial muscles, smart actuator systems and chromic windows with tunable transparency.

Published work has also highlighted polymer composites filled with metal as an interest for many fields of engineering. This interest derives from the fact that the electrical characteristics of such composites can be made close to the properties of metals, whereas the mechanical properties and processing methods are typical for plastics.

2.2 Electrical Conductivity of Composites; Measurement

Probably the earliest work that discusses the differences between the theoretical percolation probability and measured electrical conductivity appears in [6]. In this paper

they reported the results of an experiment to determine the bulk conductivity of a sheet of colloidal graphite paper with holes randomly punched in it. It was found that the conductivity dropped to zero much less sharply than the percolation probability, near the critical concentration of the holes. The reason for this phenomenon is that near the critical concentration, a lot of the paths become constricted and thus contribute little to the electrical conductivity. They suggest that the conductivity should go to zero less abruptly than the theoretical percolation probability even in a three dimensional system. It is also suggested that it would be more appropriate to compare the mobility of an electron in a disordered system with the conductivity than with the theoretical percolation probability. In summary, they concluded that the behavior of the conductivity is found to be quite different from that of the theoretical percolation probability.

One of the early references to multifunctional materials appears in [7] where they investigate both the electrical conductivity and mechanical stiffness of a polymer reinforced with cellulose whiskers. This work built on previous work in 1995, [8] illustrating mechanical percolation effects. In both papers, the authors comment on the inability of theoretical parameters in percolation models to capture experimental work. In the 1995 paper high aspect ratio whiskers were used, further emphasizing that microstructural effects, beyond connectivity, are important.

In [9] experiments were performed which demonstrated the percolation phenomena of polymers filled with metal powders, iron, copper and nickel respectively. They investigated the effect of the type of matrix and the filler distribution on conductivity. They authors used percolation models but found that theoretical models were not always a good match for experiment, and for some polymers percolation effects were not seen. They suggest that the percolation threshold depends on both particle shape and spatial distribution, which can be influenced by the polymer. The paper discusses the possibility of double percolation, conductivity due, first, to the connected filler

phase, and second, to connectivity of regions of the polymer which contain the iron particles. They define a key parameter to modeling both electrical and thermal behavior is the packing factor.

More recently, the authors in [10] investigated mechanical and electrical percolation effects on composites made by metal-ion implantation, gold and titanium, in PDMS. This paper is of particular interest because both electrical and mechanical properties are measured on same samples, and thus percolation theory is applied here to two different properties. It clearly demonstrates that the parameters for the percolation model when applied to different properties are not the same. The model material system used in this thesis is based on the titanium implanted PDMS material experimentally characterized in [10]. Details of the experiments and results from this work are provided in Chapter 6.

2.3 ELECTRICAL CONDUCTIVITY OF COMPOSITES; MODELING

Chapter 2 provides a progression from the earliest effective medium models, through percolation models, to the generalized effective medium model for electrical conductivity. The GEM model, [11], described in Chapter 2 was particularly significant in that it has also been extended to use modeling mechanical percolation [12]. Here additionally modeling approaches are discussed.

In [13], approximations as applied to linear composites, i.e., to those materials in which there is a linear relation between a curl-free electric field and a divergence-free current density, were studied. This provides the formal basis for using effective medium approaches but also opens up the door to using micromechanics composites models to capture composite conductivity. The Landauer-Bruggeman effective medium approximation, described in this work, has been a basis for a vast number of studies of macroscopically inhomogeneous media. The authors believe that as more composite microstructures are developed on an even smaller scale, this type of

approach will become more valuable.

Uvarov, in [14], proposed using a mixing rule for the predicting the conductivity of composites. Their model is an extension of the classic rule of mixtures formulation for the mechanical stiffness of composites.

Qiao and Brinson [15] used a finite element model of random circular inclusions, surrounded by an interface region to illustrate the changes in viscoleastic properties due to percolation effects that are achieved by a percolating interface region.

The most significant prior use of a micromechanics approach, was used in [16]. Where the well known composites cylinder model was used to model the effects of carbon nanotubes in a nonconducting polymer.

In this work the well known composite cylinder micromechanics model was used to study the impact of the effects of electron hopping and the formation of conductive networks on the electrical conductivity of CNT-polymer nanocomposites. The composite cylinders model uses a layered cylinder as a nanoscale representative volume element (RVE) where the effects of electron hopping are introduced in the form of a continuum interphase layer, resulting in a distinct percolation concentration associated with electron hopping. Electron hopping is a nanoscale effect associated with the ability of electrons to transfer from one CNT to another known without the rods being in direct contact. Changes in the aspect ratio of the nanoscale RVE are used to reflect the changes in nanocomposite conductivity associated with the formation of conductive networks due to the formation of nanotube bundles.

Measurements of the electrical conductivity of polymers containing CNTs have shown even greater increases (seven or more orders of magnitude relative to the neat polymer) at very low CNT concentrations, and demonstrate a sharp increase in conductivity over a very small range of CNT concentrations. Some explanations for the extremely low percolation concentrations are the dispersion of the CNTs within the polymer matrix resulting in the formation of conducting networks of CNTs and

the nanoscale effect of electron hopping. The transfer of electrons associated with this nanoscale effect can occur intra-tube or from one CNT to another, and is noted to be dependent on the separation distance between the tubes (or parts of the same tube) and on the material in between them [17].

The micromechanics model is based on the Mori-Tanaka and composite cylinders methods, and considers the nanocomposite to consist of randomly oriented CNTs well dispersed in the polymer matrix, with 1/3 of the CNTs being metallic. The Mori-Tanaka method is a micromechanics averaging method that accounts for interactions among CNTs by modifying the components of the average electric field from their dilute approximation values. The composite cylinder model is used to account for the hollow nature of the CNTs and also to introduce the effects of electron hopping into the micromechanics model through an interphase layer. The composite cylinders method is based on the application of a set of homogeneous boundary conditions to both the composite cylinder assemblage of the nanoscale RVE and to an equivalent homogeneous effective medium. In accordance with a given homogeneous boundary condition, an admissible potential field is assumed for each layer of the composite cylinder assemblage. The admissible potential fields satisfy both the boundary conditions and the conservation of charge equation. The effects of the formation of conductive networks are modeled through changes in the aspect ratio of the CNTs which are bounded by the assumption of infinitely long CNTs corresponding to conductive paths spanning the entire specimen and therefore indicative of complete percolation. For modeling purposes, the boundary value problem is dependent on the microstructure consisting of randomly oriented, straight CNTs which have a surrounding interphase layer intended to capture the effects of electron hopping. This introduces two additional parameters into the micromechanics model, the interphase thickness and the interphase conductivity. For a given set of boundary conditions, the electric potential can be determined from the conservation of charge equation.

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The major assumption for the microscale RVE is that the CNTs are well-dispersed and randomly oriented in a matrix material. The effective electrical conductivity for the microscale RVE is determined by treating each orientation of a given CNT as a separate material phase, and averaging over all possible orientations in a consistent manner such that the interactions amongst the various orientations of CNTs are accounted for. The authors have noted that through the use of the composite cylinders method, one can define concentration tensors for each layer in accordance with the generalized self-consistent, the self-consistent, or the Mori-Tanaka methods. The resulting micromechanics method would thus be considered a single step approach as it would be no longer necessary to obtain an effective CNT-interphase before obtaining the effective nanocomposite properties. While such a single step approach offers a more direct method for determining the effective nanocomposite properties, it is more cumbersome to implement than the two step approach described here.

Fralick et al., in [18], used a computational micromechanics model in a Monte Carlo simulation framework to more accurately describe microstructure and local mechanical effects that influence apparent mechanical percolation. In this thesis this approach is adopted to model electrical conductivity.

CHAPTER 3

DERIVATIONS OF MODELS FOR ELECTRICAL CONDUCTIVITY

Models for electrical conductivity of composites began being developed in the nineteenth century. What follows is a progression of the early models, from those based on first principle physics, developed into effective medium models, to the contrasting models from percolation theory and finally to models that combine elements of effective medium theory with percolation. We shall study some of the early models and come to the current models based on the effective medium theory and percolation theory. The notation used in the following presentation have been adapted from [19]

3.1 MODELS FOR DIELECTRIC CONSTANTS

The Lorenz Sphere Problem

Consider a dielectric material, with dielectric constant ϵ and uniform dipole moment, which is subjected to a constant electric field, E. A spherical domain between atoms or molecules is considered. The net electric field E^t in the sphere is expected to be larger than the applied field by an amount E_p and is given by,

$$E^t = E + E_p \qquad (3.1)$$

The relation between E^t and E can be written as,

$$E^t = \frac{E}{\left(1 - \frac{N\alpha}{3\epsilon_0}\right)} \tag{3.2}$$

where N is the number of elemental dipole moments, α is the polarizability, and ϵ_0 is the dielectric constant of free space. The dielectric constant of free space, ϵ_0, and the electric susceptibility, X_e, are related as

$$\epsilon_o = \frac{\epsilon}{1 + X_e} \tag{3.3}$$

The relative dielectric constant, ϵ_r can be written in terms of the dielectric constant of free space, ϵ_0, the dielectric constant of the material and the electric susceptibility as,

$$\epsilon_r = \frac{\epsilon}{\epsilon_o} = 1 + X_e \tag{3.4}$$

The polarizability α and relative dielectric constant ϵ_r, are related as

$$\alpha = \frac{3\epsilon_o(\epsilon_r - 1)}{N(\epsilon_r + 2)} \tag{3.5}$$

Therefore, relation between E^t and E can be rewritten in terms of ϵ_r as,

$$E^t = \frac{(\epsilon_r + 2)}{3}E \tag{3.6}$$

Considering an applied axial electric field, the magnitude of E_p along the x_1 and x_2 directions is zero; therefore, only the component of E_p in the x_3 direction needs to be considered, i.e.,

$$E_p = \frac{P}{3\epsilon_o} \tag{3.7}$$

where P is the polarization.

For isotropic materials, P is proportional to the field E as:

$$P = \epsilon_o X_e E \tag{3.8}$$

The model above uses a formulation known as "Lorentz-Lorenz" formula. The model is is called "Lorentz sphere", in honor of the physicist, Lorentz, who summarized the formulae of his predecessors to establish the model.

Maxwell's Formula

A second model was then developed, [20], as an extension to the case where the filler material has a dielectric constant ϵ_2 and is embedded as spheres in a matrix material with constant ϵ_1. The effective dielectric constant ϵ_c of this composite can be written as,

$$\frac{\epsilon_c}{\epsilon_1} = \frac{1 + 2\frac{N\alpha}{3\epsilon_1}}{1 - \frac{N\alpha}{3\epsilon_1}} \tag{3.9}$$

In this model, the polarizability α is now defined by,

$$\alpha = 3\frac{\epsilon_1(\epsilon_2 - \epsilon_1)}{\epsilon_2 + 2\epsilon_1}V \tag{3.10}$$

where V is the total volume of filler material in a sphere. If the spheres occupy a volume fraction f and N is interpreted as the number of the spheres per unit volume,

$$f = NV \tag{3.11}$$

Using the above equations, the effective dielectric constant can be obtained as,

$$\epsilon_c = \epsilon_1 \frac{1 + 2f\frac{(\epsilon_2 - \epsilon_1)}{(\epsilon_2 + 2\epsilon_1)}}{1 - f\frac{(\epsilon_2 - \epsilon_1)}{(\epsilon_2 + 2\epsilon_1)}} \tag{3.12}$$

Bruggeman's Symmetric Formula

Further extending the model to the case of two materials (ϵ_1, ϵ_2) embedded in a matrix material (ϵ_c), results in a model where each phase can be viewed as an inclusion having polarizabilities (α_1, α_2). The polarization P of the material created by these two different dielectric phases is given by,

$$P = (N_1 \alpha_1 + N_2 \alpha_2) E^t. \tag{3.13}$$

If P is integrated over the entire composite domain, it vanishes because the electric field in the background composite material is the same as the local total field, E^t. This requires the following condition is true,

$$N_1 \alpha_1 + N_2 \alpha_2 = 0. \tag{3.14}$$

Therefore, α_1 and α_2 are

$$\alpha_1 = \epsilon_c \frac{3(\epsilon_1 - \epsilon_c)}{(\epsilon_1 + 2\epsilon_c)} V_1 \tag{3.15}$$

$$\alpha_2 = \epsilon_c \frac{3(\epsilon_2 - \epsilon_c)}{(\epsilon_2 + 2\epsilon_c)} V_2 \tag{3.16}$$

Using these equations, results in what is known as Bruggeman's symmetric formula, [21] for the effective electrical conductivity, ϵ_c of the composite, which is written as

$$f_1 \frac{(\epsilon_1 - \epsilon_c)}{(\epsilon_1 + 2\epsilon_c)} + f_2 \frac{(\epsilon_2 - \epsilon_c)}{(\epsilon_2 + 2\epsilon_c)} = 0 \tag{3.17}$$

This equation is referred to as symmetric because switching the two materials does not change the function.

3.2 ELECTRICAL CONDUCTIVITY

The dielectric constant, ϵ_r, is also known as the static relative permittivity, i.e., at zero frequency. It is a complex value. Absolute permittivity is defined as

$$\epsilon_0 \epsilon_r = \epsilon' - i\epsilon'' \tag{3.18}$$

Effective electrical conductivity, σ_e, is then defined as

$$\sigma_e = \sigma_s + \omega \epsilon'' \tag{3.19}$$

This relationship allowed researchers to re-derive Bruggeman's symmetric formula in terms of conductivities resulting in an effective medium theory for conductivity,

$$f_1 \frac{(\sigma_1 - \sigma_m)}{(\sigma_1 + 2\sigma_m)} + f_2 \frac{(\sigma_2 - \sigma_m)}{(\sigma_2 + 2\sigma_m)} = 0 \tag{3.20}$$

where σ_1, is the conductivity of the included phase, σ_2 is the conductivity of the matrix material, and σ_m is the conductivity of the homogenized, composite medium. The formula can be solved explicitly for the conductivity of the composite, σ_m, as

$$\sigma_m = \frac{1}{4}[\eta + (\eta^2 + 8\sigma_1\sigma_2)^{1/2}] \tag{3.21}$$

where,

$$\eta = (3f_2 - 1)\sigma_2 + (3f_1 - 1)\sigma_1. \tag{3.22}$$

This is the effective medium approximation for electrical conductivity of a composite.

3.3 PERCOLATION THEORY

Percolation theory is well developed based on lattice grid models [22]. These mathematical and simulation studies have long been connected to experimental observation of the electrical conductivity of composites. In [23] the conductivity of a a random resistor network was evaluated using Monte Carlo simulations based on the Kirchoff

current law. In this work they reported that conductivity near the a threshold value was well described by

$$\sigma(v) \sim (v - \phi_c)^t \tag{3.23}$$

where, σ is conductivity, v is volume fraction and ϕ_c is the percolation threshold. This power law form has been widely adopted to model percolation behavior. The most common modification is to add a scaling factor, σ_0 i.e.,

$$\sigma(v) = \sigma_0(v - \phi_c)^t \tag{3.24}$$

which often varies depending on whether the volume fraction is above or below the percolation threshold.

3.4 GENERAL CONDUCTION LAWS

The effective medium theories described above are valid for the full range of volume fractions but they do not the capture probabilistic effects such as the formation of a percolated microstructure. Percolation models are generally only value above and near the percolation threshold. The next efforts in modeling the electrical conductivity of composites focused on combining elements of both approaches.

Extended Percolation

Percolation models were adapted to include the full range of volume fractions. In [24, 25] macroscopic conductivity is given by

$$\sigma_m(v) = \begin{cases} \sigma_0(v - \phi_c)^t & \text{for } v > \phi_c \\ \sigma_0(\phi_c - v)^{-s} & \text{for } v < \phi_c \\ \sigma_0(\sigma_1/\sigma_0)^u & \text{for } v \approx \phi_c \end{cases}$$

where v is volume fraction, σ_0, σ_1, ϕ_c are the conductivity of the matrix, conductivity

of the included phase and percolation threshold, respectively, and

$$u = \frac{1}{t+s}.$$ (3.25)

Generalized Effective Medium Theory

A direct combination of effective medium theories with percolation theory was proposed by McLachlan et al. [26] and is known as the Generalized Effective Medium Theory (GEM). The GEM equation combines aspects of both percolation and Bruggeman's symmetric effective medium model. The effective electrical conductivity of the whole range of conductor volume fractions, including the conductor-insulator transition region around percolation threshold are described by

$$(1-f)\frac{\sigma_C^{1/t} - \sigma_M^{1/t}}{\sigma_C^{1/t} + A\sigma_M^{1/t}} + f\frac{\sigma_I^{1/t} - \sigma_M^{1/t}}{\sigma_I^{1/t} + A\sigma_M^{1/t}} = 0$$ (3.26)

where σ_C, σ_I, σ_M are the conductivities of the conductor, insulator and composite, and f is the volume fraction. The constant A is described in terms of the percolation threshold, ϕ_c, and can be related to the de-magnitizing factors of the matrix (conductor). L_m and insulator (particles), L_p.

$$A = \frac{1 - \phi_c}{\phi_c} = 1 - \frac{L_m}{L_p}$$ (3.27)

CHAPTER 4

MICROMECHANICS MODEL

Micromechanics of materials is the analysis of composites at the level of the individual constituents. Heterogeneous materials, such as composites, solid foams and polycrystals, consist of clearly distinguishable constituents or phases that show different mechanical and physical material properties. This is in contrast to alloys or blends.

Micromechanics models predict the response of the composite on the basis of the geometries and properties of the individual phases, given the material properties of the constituents. The best models are developed from physical and mathematical principles and validated through comparison to experimental data.

4.1 EFFECTIVE PROPERTIES

The majority of micromechanics of materials are based on continuum mechanics and the assumption of continuum length scales. Although it can be argued that continuum models are not strictly valid for the study of nanocomposites, [27, 28], the literature provides a number of examples where continuum models have proved surprisingly accurate in modeling these materials, [29]. In addition to the mechanical responses of inhomogeneous materials, micromechanical models, based on homogenization principles can be used to model other effective field properties. For example, consider the equation

$$\langle F(r) \rangle = K_e \langle G(r) \rangle \tag{4.1}$$

where F represents some generalized flux, K_e represents the effective tensor property, G represents some generalized gradient and the angular brackets denote an average. For mechanics this equation can be rewritten as

$$\bar{\sigma} = C^e \bar{\epsilon} \tag{4.2}$$

where $\bar{\sigma}$ is the average stress tensor, force per unit area and so a flux, C^e is the effective stiffness tensor and $\bar{\epsilon}$ is the linearized strain tensor.

In a similar fashion, effective conductivity can be written in the same mathematical form as eqn. 4.1 as

$$\bar{J} = \sigma^e \bar{E} \tag{4.3}$$

where $\bar{J}$ is the average current density or electric flux vector, σ^e is the effective electrical conductivity tensor, $\bar{E}$ is the average electric field vector. the most significant difference between eqns. 5.1 and eqn. 5.2 is that the effective stiffness tensor is a 4th order tensor and the effective conductivity tensor can be either a 2nd order diagonal tensor or a scalar. To complete the comparison, ϵ is a gradient of displacement, E is the gradient of electrical potential.

4.2 GENERALIZED METHOD OF CELLS

Because of the mathematical similarity of the problems, in this work it is proposed to use a computational micromechanics model to predict the effective electrical conductivity of a polymer nanocomposite. The micromechanics model allows consideration of the details of the microstructure, phase volume fractions, orientations, sizes and shapes of the included phase, spatial distribution of the phase domains, and phase properties. By using the micromechanics model in a Monte Carlo simulation framework, probabilistic effects, such as random microstructures and percolation effects, can be captured.

In this work, the computational micromechanics model known as the Generalized Method of Cells (GMC), [30] is used. GMC is a periodic unit cell model that uses a rectangular repeating unit cell (RUC), composed of multiple subcells, as the representative volume element (RVE) for a periodic microstructure. Most random composite materials can be characterized as a statistical arrangement of the constituents, therefore, the methods of micromechanics are typically based on the concept of the representative volume element (RVE). An RVE is the smallest volume over which a measurement or can be made that will yield a property value that is representative of the whole.

The arbitrary number of subcells, each assigned properties of one of the composite phases, provides a significant amount of microstructural detail. The homogenization process in GMC connects the material microstructure, through periodic boundary conditions, to an equivalent homogeneous material with a set of continuum level equations; resulting in a prediction of the effective properties. Specific boundary conditions enforce continuity of displacements and tractions across subcell boundaries and between RUCs. As these conditions are satisfied in an average sense, integrating over the boundaries, the effect of the rectangular geometry, i.e. sharp corners, is minimal in the prediction of effective properties. In what follows the general description of the underlying theory of GMC has been adapted to the notation appropriate for electrical conductivity.

The GMC model begins with a repeating unit cell. The unit cell is divided into $(N_\alpha \times N_\beta \times N_\gamma)$ rectangular subcells, where the number of subcells is determined by the detail needed to describe the microstructure. Each subcell is homogeneous and contains one of the constituent components of the heterogeneous material. A subcell is denoted by the ordered triple (α, β, γ) that identifies its x_1 position, from bottom to top, its x_2 position, left to right, and its x_3 position. Each subcell volume is given by $d_\alpha \times h_\beta \times l_\gamma$.

GMC establishes a relationship between the average global electric field in the composite and the local subcell electric field. This relationship is known as a concentration tensor that can be used to predict the effective properties of the composite. Once the subcell electric fields are known, the average subcell electric flux can be calculated using known subcell constitutive laws. Global fluxes and fields are volume averages of subcell values.

In each subcell (α, β, γ) the average flux is defined as

$$\bar{J}^{\alpha\beta\gamma} = \sigma^{\alpha\beta\gamma}\bar{E}^{\alpha\beta\gamma} \tag{4.4}$$

Average electric fields (referred to in the following as just fields), in the composite are given by

$$\bar{E} = \frac{1}{dhl}\sum_{\alpha=1}^{N_\alpha}\sum_{\beta=1}^{N_\beta}\sum_{\gamma=1}^{N_\gamma}d_\alpha h_\beta l_\gamma \bar{E}^{\alpha\beta\gamma} \tag{4.5}$$

Average flux in the composite can be defined by

$$\bar{J} = \frac{1}{dhl}\sum_{\alpha=1}^{N_\alpha}\sum_{\beta=1}^{N_\beta}\sum_{\gamma=1}^{N_\gamma}d_\alpha h_\beta l_\gamma \bar{J}^{\alpha\beta\gamma} \tag{4.6}$$

where d, h and l are the dimensions of the total repeating unit cell, and d_α, h_β and l_γ are the dimensions of subcell (α, β, γ).

The relationship between the global and subcell fields is defined by a system of equations that is constructed by requiring that potentials and fluxes are continuous across unit cell and subcell boundaries. The components of the potential ϕ_i at the interfaces within the unit cell and between unit cells must be continuous so that for $\alpha = 1, ...N_\alpha$; $\beta = 1, ...N_\beta$; $\gamma = 1, ...N_\gamma$,

$$\phi_i^{(\alpha\beta\gamma)}\big|_{\bar{x}_1^\alpha = d_\alpha/2} = \phi_i^{(\hat{\alpha}\beta\gamma)}\big|_{\bar{x}_1^{\hat{\alpha}} = d_{\hat{\alpha}}/2} \tag{4.7}$$

$$\phi_i^{(\alpha\beta\gamma)}\big|_{\bar{x}_2^\beta = h_\beta/2} = \phi_i^{(\alpha\hat{\beta}\gamma)}\big|_{\bar{x}_2^{\hat{\beta}} = h_{\hat{\beta}}/2} \tag{4.8}$$

$$\phi_i^{(\alpha\beta\gamma)}\big|_{\bar{x}_3^\gamma = l_\gamma/2} = \phi_i^{(\alpha\beta\hat{\gamma})}\big|_{\bar{x}_3^{\hat{\gamma}} = l_{\hat{\gamma}}/2} \tag{4.9}$$

enforcing the periodic boundary conditions assumed in the model, as

$$\hat{\alpha} = \begin{cases} \alpha + 1 & \text{when } \alpha < N_\alpha \\ 1 & \text{when } \alpha = N_\alpha \end{cases} ; \hat{\beta} = \begin{cases} \beta + 1 & \text{when } \beta < N_\beta \\ 1 & \text{when } \beta = N_\beta \end{cases} ; \hat{\gamma} = \begin{cases} \gamma + 1 & \text{when } \gamma < N_\gamma \\ 1 & \text{when } \gamma = N_\gamma \end{cases}$$

(4.10)

These conditions can be written in matrix form as

$$A_G E_s = D\bar{E} \tag{4.11}$$

where $\bar{E} = (\bar{E}_{11}, \bar{E}_{22}, \bar{E}_{33})$ and $E_s = \bar{E}^{111}, ..., \bar{E}^{N_\alpha N_\beta N_\gamma}$.

Continuity of flux requires

$$\begin{aligned} \bar{J}_{11}^{\alpha\beta\gamma} &= \bar{J}_{11}^{\hat{\alpha}\beta\gamma} \\ \bar{J}_{22}^{\alpha\beta\gamma} &= \bar{J}_{22}^{\alpha\hat{\beta}\gamma} \\ \bar{J}_{33}^{\alpha\beta\gamma} &= \bar{J}_{33}^{\alpha\beta\hat{\gamma}} \end{aligned}$$

(4.12)

These equations can be written in the matrix form as

$$A_M(E_s) = 0 \tag{4.13}$$

where A_M contains the conductivity properties of the subcell material. From above equations, we get

$$\bar{A}E_s = K\bar{E} \tag{4.14}$$

where

$$\bar{A} = \begin{pmatrix} A_M \\ A_G \end{pmatrix} \bar{D} = \begin{pmatrix} A_M \\ 0 \end{pmatrix} K = \begin{pmatrix} 0 \\ D \end{pmatrix} \tag{4.15}$$

For the case considered here, we get

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$$\bar{A}E_s = K\bar{E} \tag{4.16}$$

Finally, we establish the effective conductivity of the composite

$$\bar{J} = B^*\bar{E} \tag{4.17}$$

where B^* is the effective electrical conductivity tensor for the composite.

For a given set of boundary conditions at the macroscale, the electric potential ϕ, can be determined from the conservation of charge equation, which in the case of steady state conditions has the form:

$$\nabla J = 0 \tag{4.18}$$

where the electric flux vector, J, is assumed to obey Ohm's law, which is given by,

$$J = \sigma E \tag{4.19}$$

and where, again, σ is the effective electrical conductivity for the nanocomposite determined from the microscale representative volume element, with input from the nanoscale RVE, and E is the electric field vector which can be expressed in terms of the electric potential, ϕ, by

$$E = -\nabla \phi \tag{4.20}$$

CHAPTER 5

COMPARISON OF ELECTRICAL AND MECHANICAL

MODEL PREDICTIONS

To use the Generalized Method of Cells, GMC, framework for molding electrical conductivity requires, as presented in Chapter 4, replacing the generalized Hooke's Law for the elastic properties of a composite

$$\sigma = C^e \epsilon, \tag{5.1}$$

where C^e is the 4th order effective stiffness tensor of the composite, with

$$J = \sigma^e E, \tag{5.2}$$

where J is the electric flux, E is the electric field, and σ^e is the 2nd order effective conductivity tensor of the composite.

The inverse of the elastic stiffness tensor, C, is the elastic compliance tensor, $S = C^{-1}$, which can be written in terms of the engineering constants, E, G and ν as,

$$S = \begin{bmatrix} \frac{1}{E} & -\frac{\nu}{E} & -\frac{\nu}{E} & 0 & 0 & 0 \\ -\frac{\nu}{E} & \frac{1}{E} & -\frac{\nu}{E} & 0 & 0 & 0 \\ -\frac{\nu}{E} & -\frac{\nu}{E} & \frac{1}{E} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G} \end{bmatrix}$$

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The conductivity tensor is given by

$$\sigma = \begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{bmatrix}$$

or the scalar σ for an isotropic material.

By comparing the two, it can be seen that if the Poisson's ratio in the compliance tensor is set equal to zero

$$S = \begin{bmatrix} \frac{1}{E} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{E} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{E} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G} \end{bmatrix}$$

then the stiffness tensor is easily found as

$$C = \begin{bmatrix} E & 0 & 0 & 0 & 0 & 0 \\ 0 & E & 0 & 0 & 0 & 0 \\ 0 & 0 & E & 0 & 0 & 0 \\ 0 & 0 & 0 & G & 0 & 0 \\ 0 & 0 & 0 & 0 & G & 0 \\ 0 & 0 & 0 & 0 & 0 & G \end{bmatrix}$$

and the upper block 3×3 block matrix equated to the conductivity tensor. The shear values can be ignored since the model considers at most orthotropic materials which exhibit no shear-normal coupling.
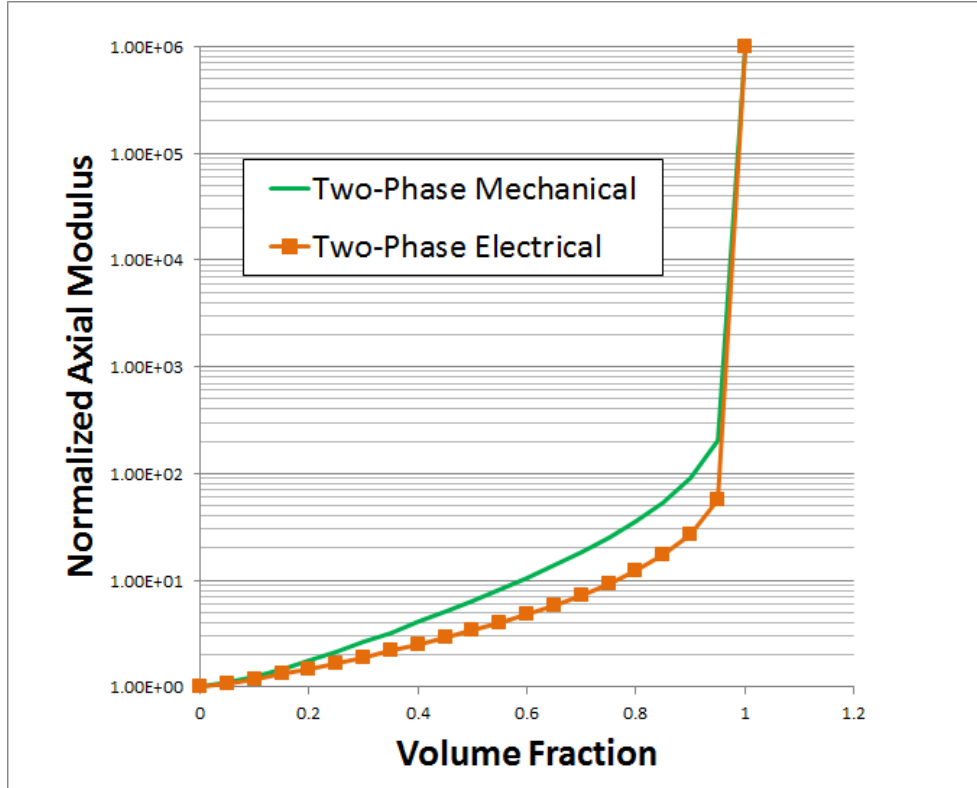
Figure 5.1: Mechanical vs Electrical normalized axial modulus, two-phase composite

5.1 EFFECT OF MODEL ADAPTATION

In order to demonstrate the effect of this adaptation, materials with triply periodic microstructures were modeled using the same numeric values for moduli but with either a non-zero (mechanical) or zero (electrical) Poisson's ratio. The GMC built-in square packing arrangement was used. Both the two phase, particle and matrix, and the three phase, particle interface and matrix were considered.

Figure 5.1 compares predictions of the model using the original mechanical formulation and the modified electrical formulation for a two phase composite in a square packing arrangement. Figure 5.2 compares predictions of the model using the original mechanical formulation and the modified electrical formulation for a three phase composite in a square packing arrangement. Beyond a volume fraction of approximately 0.30, given the constraint that the interface thickness remain half of the particle, the
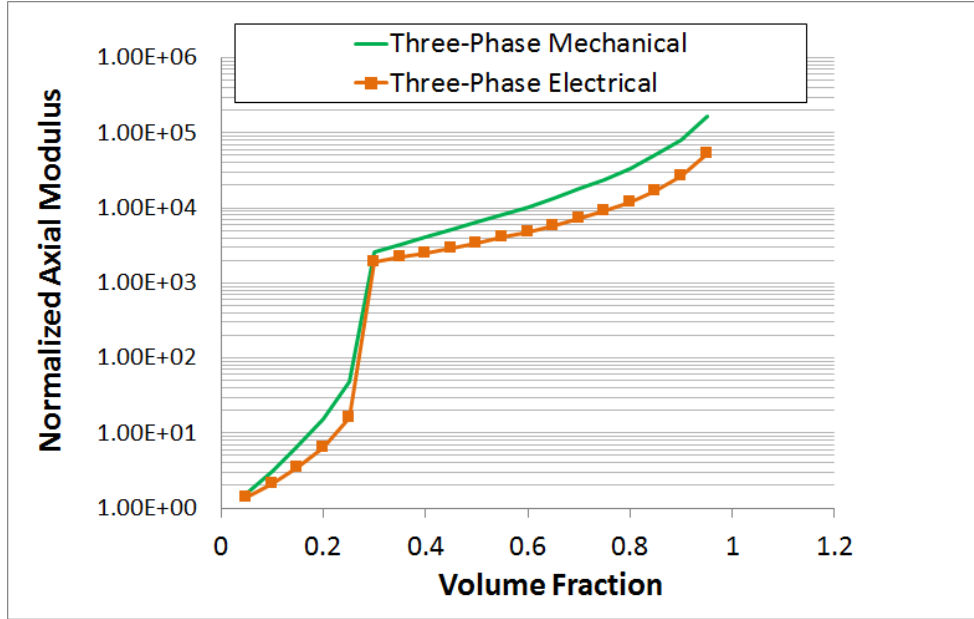
25

Figure 5.2: Mechanical vs Electrical normalized axial modulus, three-phase composite

matrix material must be completely gone. To increase the particle volume fraction further, at this point the interface volume fraction must be reduced. In this deterministic model, an artificial pseudo-percolation threshold has been created, particles are connected through interface material. To model subsequent effects, a two phase GMC square packing model is used, with just particle and interface material.

CHAPTER 6

MODEL MATERIAL SYSTEM

In order to provide a basis for comparison, the model proposed in this work is applied to an experimental model material system.

In [10], the technique of metal-ion implantation of polymers was used to make polymer-metal composites. In this process metal ions are accelerated by an electric field into a solid material, here a polymer. In this paper, they used titanium and gold ions emplaned in a polydimethysiloxane(PDMS) substrate polymer.

The result of this process is the formation of metal nanoparticles in the top 10-100 nm of a polymer film and a metal/insulator composite whose electrical conductivity displays percolative behavior. What is novel about this work is that they observed percolation effects for both the Young's modulus, Y, and electrical conductivity, σ.

Cross-sectional micrographs, using a Transmission Electron Microscope (TEM), allowed detailed microstructural analysis of the implanted layers. It was found that the gold ions penetrated up to 30 nm and formed crystalline nanoparticles whose sizes increased with ion dose and energy. In contrast, titanium formed a nearly homogeneous amorphous composite with the PDMS up to 18 nm thick.

Also from TEM, the metal volume fractions in the composites could be determined. This allowed both electrical conductivity and Young's modulus to be plotted against the volume fraction. These plots showed clear percolation effects for both properties, The authors used quantitative percolation models to characterize the results. Hence, the composite's Young's modulus and conductivity could be linked directly to the implantation parameters, dose and electric field, and volume fraction.

These two effective properties are both related to the structure of the composite, therefore in the simplest model, it would be assumed that the percolation thresholds would be the same for electrical conductivity σ and for the Young's modulus Y. However, the underlying mechanisms are different for the two properties and both Y and σ are influenced by implantation induced effects. The first is the addition of metal atoms in the elastomer matrix, i.e. the increase in metal volume fraction as the dose increases, and the second is the radiation induced chemical modifications of the molecular structure of the PDMS, chemical changes.

When an energetic ion hits the PDMS, it induces changes in the chemistry of the polymer by chain-scission and cross-linking, leading to increased density and reduced molecular weight, and to higher stiffness. In this work, it was found that radiation damage of the PDMS did not have an impact on the conductivity of the composite, as the PDMS remained insulating, but it played an important role in the mechanical properties of the composite.

The article also discussed cluster formation in the metal-ion composites. The metal clusters would touch and provide an electronic conductive path, but without forming a strong mechanical bond. This allows the clusters to slide relative to one another other if strain is applied to the polymer matrix permitting for relatively large strains before losing conductivity in the composite, resulted in low degradation when cyclically stretched. The composite formed by gold ion implantations consists of gold clusters in a PDMS matrix. It was observed that the gold ions form rounded gold clusters having a crystalline structure, whose size increases with energy and with dose from 2 to 20 nm. The gold cluster size increases with the volume fraction, then saturates. One of the explanations that they offer for this phenomenon is that the clusters cease to grow once they touch, which would also correspond to a rapid increase in Y_{Comp}. Thus it was also observed that the formation of larger clusters results in percolation at a lower volume fraction than smaller clusters.

They also found that, in contrast, titanium does not form metallic clusters, but binds with the PDMS. The size of these Ti-rich regions increases with the dose and with energy. At high doses, they form a homogeneous gray layer of highly titanium doped PDMS. The reason for the lack of titanium clusters lies in its electronegativity, which is the lower than that of the PDMS constituent atoms. Consequently, titanium will bind with the PDMS rather than with itself.

Both, electrical and mechanical properties were measured on the same nanocomposite samples, and different percolation thresholds and exponents were found, demonstrated that, while percolation describes both conduction and stiffness of the composite very well, the interaction between metal nanoparticles occurs differently in determining mechanical and electrical properties.

In the current work the primary interest is in the effective electrical conductivity σ of the nanocomposite samples. The experimentally observed shows the general shape expected for percolative systems with a steep rise in the electrical conductivity σ at the percolation threshold for both composites. There was very little difference in the composite conductivity due to implantation energy, but there was a significant difference between the gold and titanium samples. The gold composites consistently displayed a lower apparent percolation threshold, $\sim 0.05 - 0.07$; the titanium samples percolated in the range of $\sim 0.11 - 0.13$.

The electrical percolation threshold is clearly distinct for the titanium and gold samples, in each case it appears independent of ion energy. Both the conductivity and the stiffness of these composites are well explained by a percolation model, however theoretical predictions for percolation thresholds did not match the experimental results and were different for the two properties, i.e., mechanical stiffness and electrical conductivity. This was clearly due to the interactions between metal nanoparticles, between particles and the matrix, and the underlying physics of each property.

Because the titanium samples showed less clustering and presented as a more

distinct composite, the data reported for these samples is used here for comparisons.

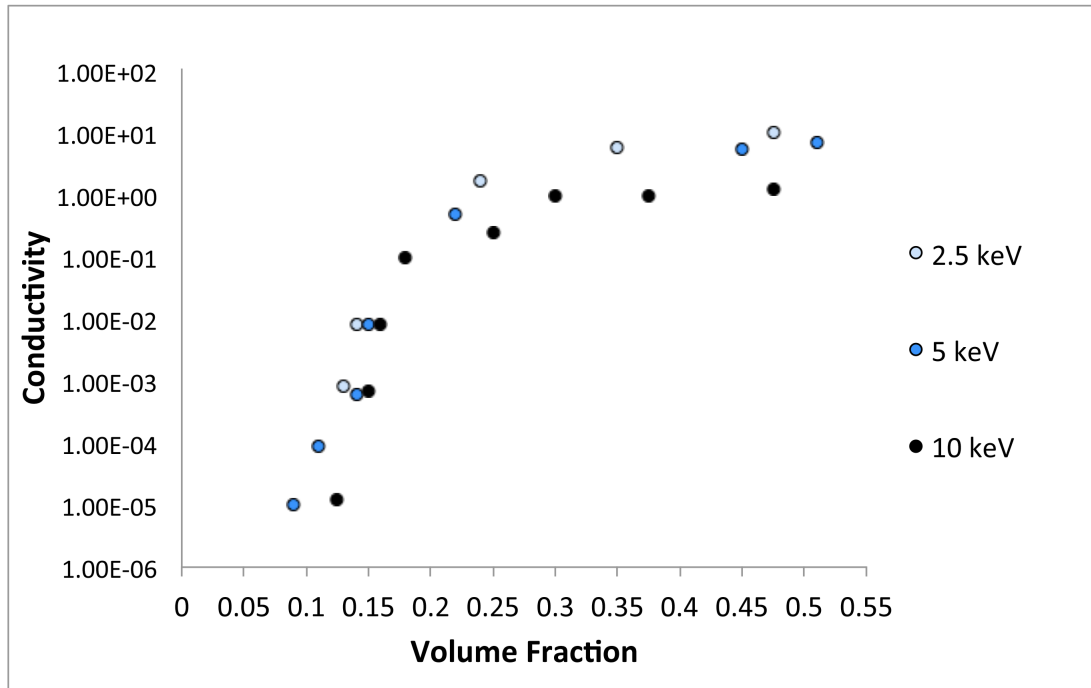Figure 6.1 is an approximation of the data presented in [10].

Figure 6.1: Electrical conductivity of titanium ions implanted at 2.5, 5, and 10 keV, from [10]

Chapter 7

Results

7.1 Baseline Model

A baseline model was based on the Titanium - PDMS material model described in [10]. In this work nanocomposites were created by the ion implementation method, by implanting gold and titanium into polydimethysiloxane(PDMS) using doses of $0.1x10^{16}$ to $5x10^{16}$ $at.cm^{-2}$, and for ion energies of 2.5, 5 and 10 keV are reported. The following parameters are used in this baseline model. The conductivity of the PDMS was assigned as 2.38×10^{-6}, the conductivity of the titanium was assigned as 2.38×10^{6}. The interface region was assigned a conductivity equal to the geometric mean of the particles and matrix, 2.38. Initially the interface thickness was assumed to be equal to half the diameter of the particles. All three materials were given a Poisson's ratio equal to zero, in order to simulate electrical conductivity.

Random microstructures were generated for use as the RUC in GMC; 300 microstructures were simulated for each volume fraction, from 0 to 0.40, which is the primary region of interest for electrical percolation, in steps of 0.05. GMC was used to approximate the composite effective conductivity for each simulated microstructure.

Figure 7.1 shows the results of simulation; minimum, mean and maximum conductivities are plotted when the interface diameter is one-half of the particle diameter. An apparent percolation threshold is observed at a volume fraction of 0.05. As in [18] this is designated as an apparent percolation threshold because a likely mechanism is a connected microstructure that forms using particles and interface, within a
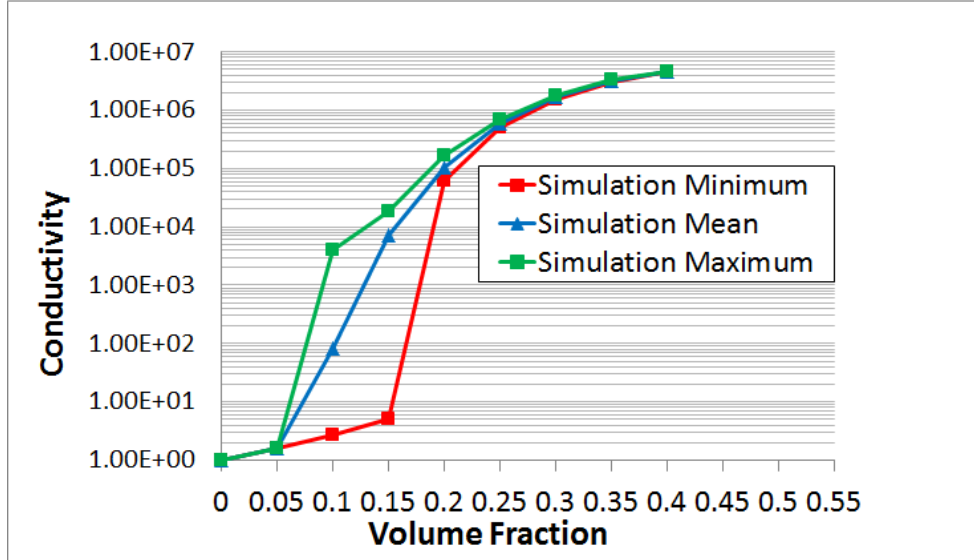
Figure 7.1: Results of Simulation; minimum, mean and maximum simulated conductivities; interface is one-half the diameter of the particle and has a conductivity equal to the geometric mean of the particle and matrix conductivity.

surrounding matrix. At these low volume fractions continuous particle stacks do not form.

7.2 Comparison to Experimental Results

Figure 7.2 compares the simulated results for the baseline model plotted with the experimental data from [10] for the titanium nanocomposite. Experimental results showed little variation in the composites based on dose, or electric field. It can be observed that the baseline model agrees closely with the original model at higher volume fractions, but the apparent percolation threshold is slightly lower than that observed in the data.

7.3 Interface Thickness

To demonstrate the influence of micromechanical structure, a second model was simulated as in fig.7.3, which illustrates the simulated minimum, mean and maximum when the interface diameter is one-third of the particle diameter. An apparent perco-
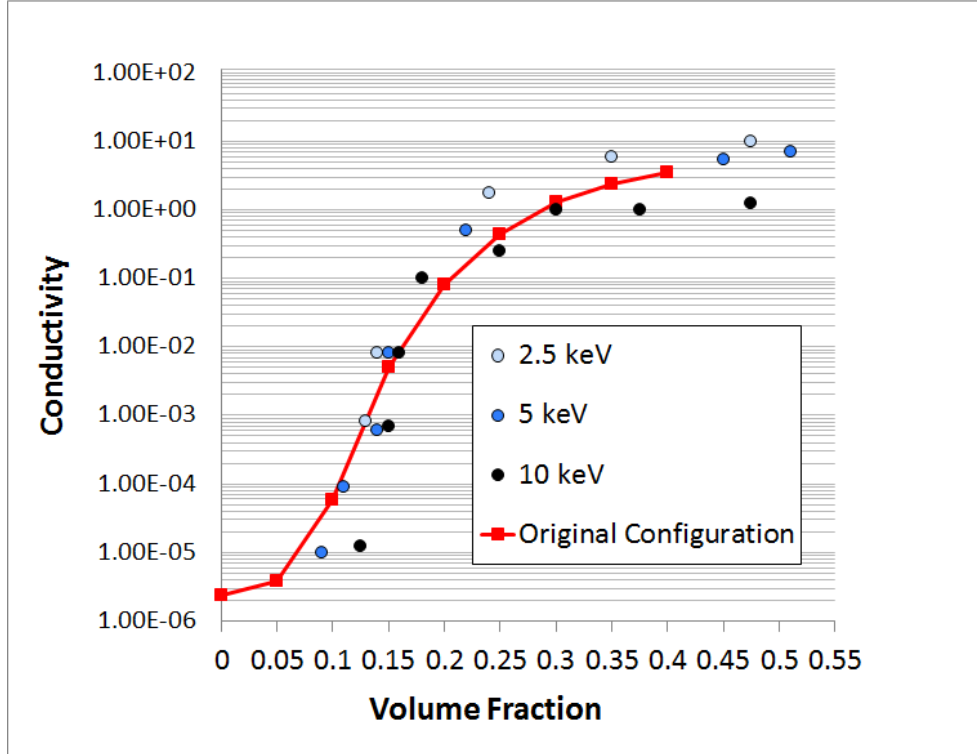
Figure 7.2: Comparison of Original Simulation Average to Experimental Results.

lation threshold is observed at a volume fraction of 0.1. The simulated results are then compared to the experimental data from [10], as in fig.7.4. It can be observed that the thin interface model more closely captures the apparent percolation threshold, but its predictions are somewhat low for the higher volume fractions.

Figure 7.5 plots simulation results which use a thin interface, equal to one third of the particle diameter, versus the baseline model, one half the particle interface. Phase properties were the same for both models. On this graph it can be observed that the apparent percolation threshold for the original interface occurs at a volume fraction of 0.05 while it occurs at 0.1 for the thin interface. This duplicates the results obtained in previous work [18], where it was reported that as the interface thickness decreases, the apparent mechanical percolation threshold increases.

A third model was constructed based on the thin interface model, but assigning the interface a higher conductivity, greater by a factor of 10. The simulated minimum,
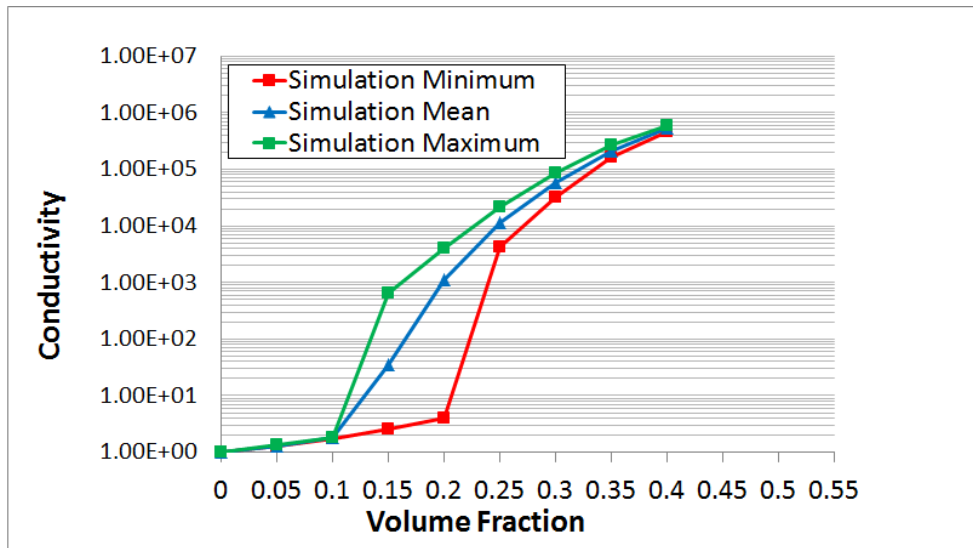
Figure 7.3: Results of Simulation; minimum, mean and maximum simulated conductivities; interface is one-third the diameter of the particle and has a conductivity equal to the geometric mean of the particle and matrix conductivity.
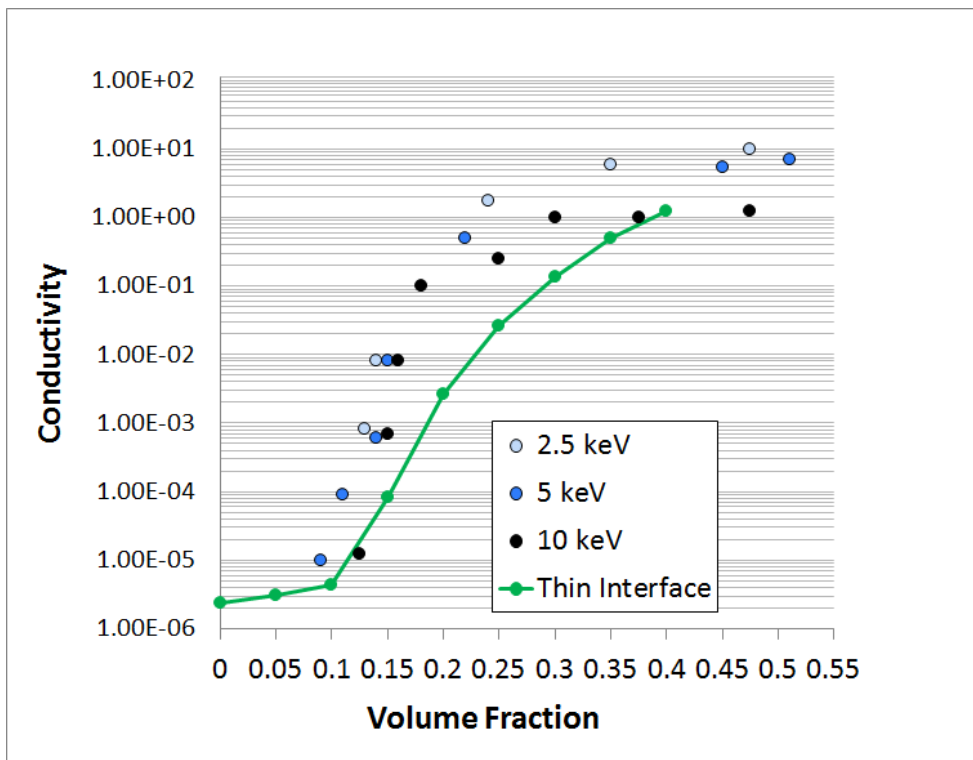

Figure 7.4: Comparison of Thin Interface Simulation Average to Experimental Results.
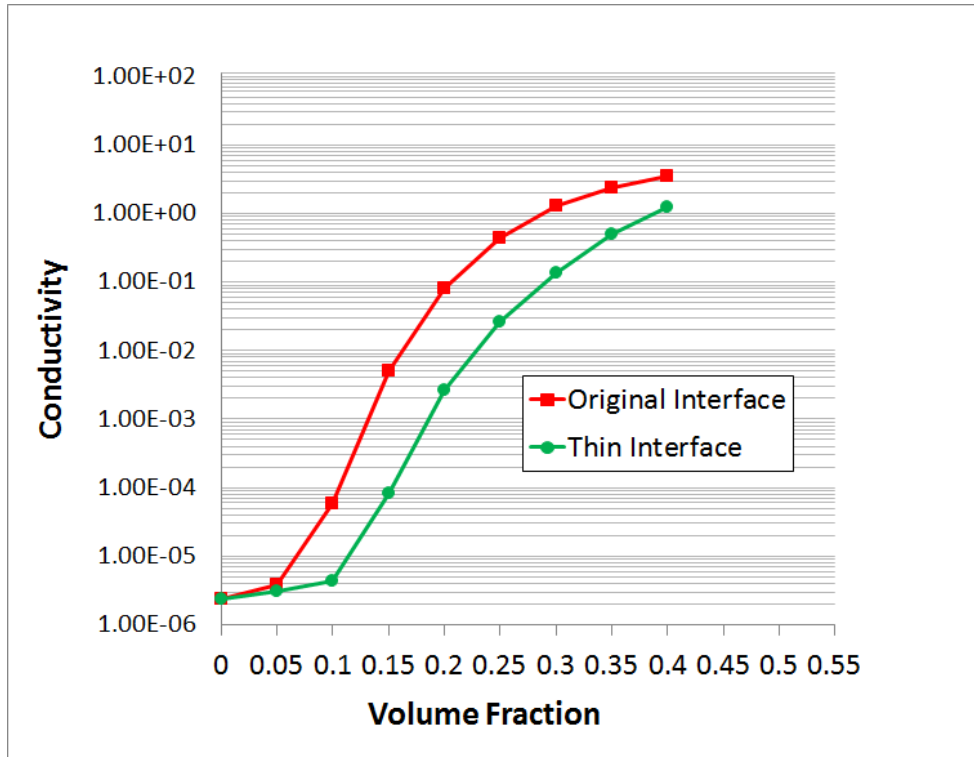
Figure 7.5: Results of Simulation; comparison of simulations when the interface is one-half the diameter of the particle and one-third the diameter of the particle.

mean and maximum is shown in fig.7.6. The simulated results are then compared to the experimental data from [10]and shown in fig.7.7. The apparent percolation threshold is a good match and the subsequent composite conductivity is somewhat better, however the trajectory of the percolation curve suggests predictions that are slightly too high.

Finally, a comparison of the three models is shown in fig. 7.8.

The original simulation parameters appear to the the best of the three cases. A finer scale of the volume fractions might be useful in refining the model, further discretization of the GMC model with an interface between 1/2 and 1/3 might also be useful.
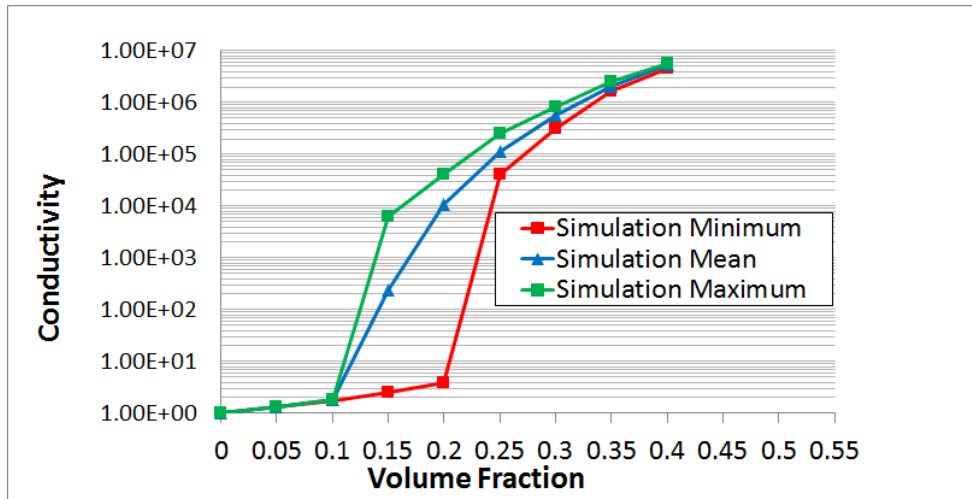
Figure 7.6: Results of Simulation; minimum, mean and maximum simulated conductivities; interface is one-third the diameter of the particle and has a higher conductivity.
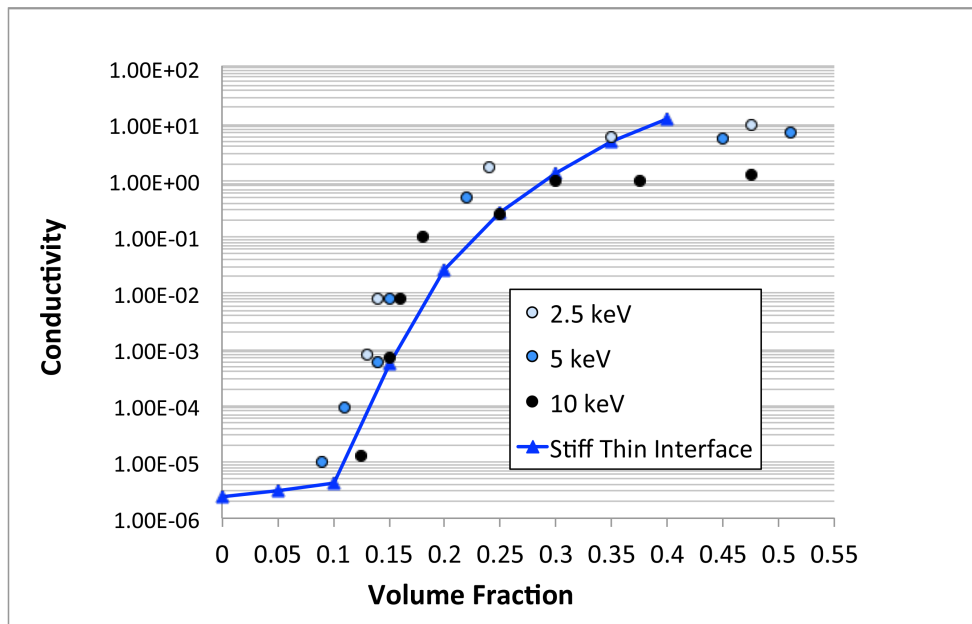

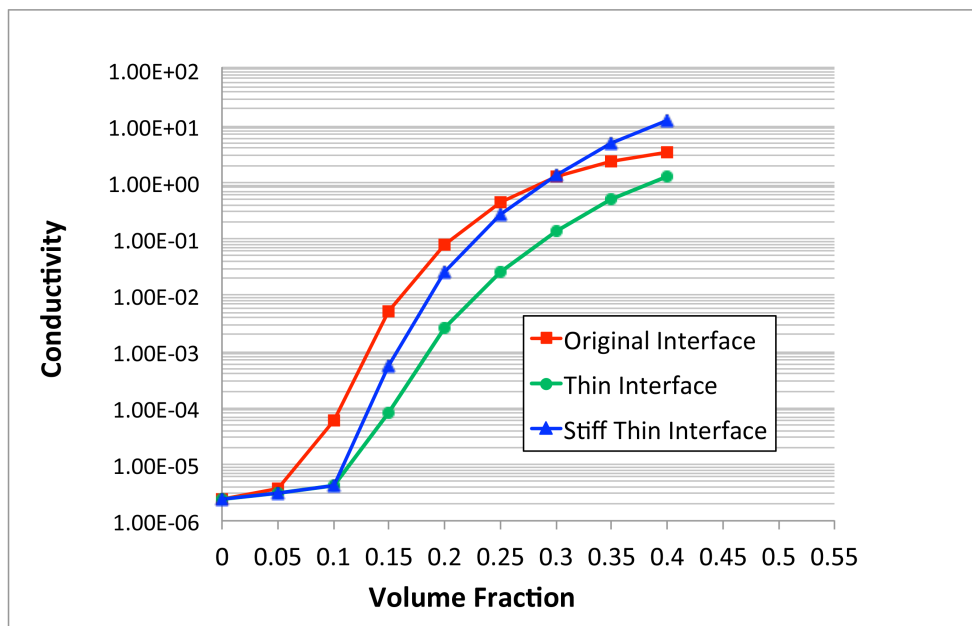Figure 7.7: Comparison of Thin, More Conductive Interface Simulation Average to Experimental Results.

Figure 7.8: Results of Simulation; comparison of simulations when the interface is one-half the diameter of the particle and when it has one-third the diameter of the particle with the original and more conductive interface.

CHAPTER 8

CONCLUSIONS

Composite materials can combine the properties of multiple constituent materials in a very advantageous manner in order to tailor properties to the application. A nanocomposite is a multiphase, solid material where one phase has at least one dimension on the order of 100 nm. Studying the behavior of these materials is very interesting and important given the potential they have in wide-ranging applications.

The challenge to modeling multi-functional properties of PNCs is that, traditionally, different models have been applied to model different properties. Mechanical properties are most often modeled using mean-field models from micromechanics; properties depend on the microstructural arrangement of the included phase, phase properties and volume fraction. Electrical conductivity has primarily been modeled using percolation theory and power-law models; properties depend on theoretical or simulation based estimates of a percolation threshold, phase properties and volume fraction. However, models of both properties, should be built on specific microstructural descriptions as well as include a probabilistic framework to capture percolation effects.

In this work, a modeling framework, developed for mechanical properties, is investigated for its applicability in modeling effective electrical composite properties. The model is used to predict the effective composite properties of a metal-polymer composite, titanium in PDMS. The results were compared to measured conductivities published in [10].

The simulation results which included an interface with a thickness equal to one

half the particle thickness, and a conductivity equal to the geometric mean of the particle and matrix, provided the best overall fit to the data. A thinner interface matched the apparent percolation threshold better, but underestimated composite conductivity at higher volume fractions. A thin stiff interface matched the apparent percolation threshold well, but overestimated the composite conductivity at higher volume fractions.

A relatively thin interface corresponds to current understandings of mechanisms such as electron hopping which allow conduction even if the particles are not directly connected. It is expected that the distances for electron hopping are relatively small ~ 10 nm. It would also be expected that the conductivity of the interface was relatively high. A finer scale of the volume fractions might be useful in refining the model, further discretization of the GMC model with an interface between $1/2$ and $1/3$ might also be useful.

The work demonstrated the usefulness of such a model for predicting the effective composite conductivity of polymer nanocomposites. The simulation framework allowed percolated and pseudo-percolated (particle interface connections) microstructures to form, and the micromechanics model provides a consistent framework for predicting the properties of each random microstructure. The significance of this modeling approach is that the same microstructures could be used to predict both mechanical and electrical properties of the composite.

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