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Polymer Nanocomposites Characterization by a Stochastic Finite Elements Representation

by

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Abstract

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This dissertation introduces a new multiscale stochastic finite element method (MSFEM) for determining the mechanical properties of polymer nanocomposites (PNC) consisting of polymers reinforced with single-wall carbon nanotubes (SWCNT). Obviously, reliable characterization of the various properties of nanomaterials such as PNC is indispensable in engineering applications. In this context, it is noted that the results reported in the literature often overestimate the actual mechanical properties of PNC reflecting uncertainty in the assumptions and approximations made. The method proposed herein uses actual experimental characterization information at the nano and micro scales to model the spatial randomness induced by the non-uniform dispersion of SWCNT in polymers, and to determine the mechanical properties of PNC.

First, the proposed method defines a material region and identifies randomness at the nanoscale. Second, it develops a random field model that quantifies the spatial randomness in PNC. Then, the method formulates a Monte Carlo finite element (FE) scheme used to solve a specific elasticity problem. This FE scheme incorporates the effects of the local mechanical properties of both phases in PNC and the size, shape, orientation, agglomeration, and dispersion of SWCNT in polymers.
The developed MSFEM is used in three applications in the dissertation. In the first, tensile test results of two PNC presented in the literature are used to derive estimates of the Young's modulus (YM) and Poisson ratio (PR). The results demonstrate the success of the proposed method in quantifying the effect of the spatial randomness on the mechanical properties of PNC. The second application uses experimental information about nanoindentation (NI) testing to numerically generate NI data which are subsequently used to compute estimates of the overall YM of PNC. The third application addresses the elastic stability of PNC structures. The computed results show the effect of incorporating SWCNT in polymers, as well as of the material randomness on the buckling loads and modes of the PNC structures.

Overall, the proposed MSFEM succeeds in modeling the effect of the spatial randomness on the mechanical properties of PNC by using actual experimental findings, and by efficiently combining information obtained at different length scales.
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I dedicate this dissertation to my mother Mrs. Eleni Kontsos.
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Chapter 1

Introduction

1.1 Motivation

Realistic modeling of the mechanical behavior of new nanocomposite (NC) materials enhances the safety and reliability of modern engineering structures, and it is the subject of this dissertation. The mechanical behavior of traditional materials, such as metals, ceramics and polymers can be significantly improved by mixing them with various reinforcement agents, such as fibers and particles of various dimensions. In the case of nanocomposites, carbon nanotubes (CNT) are dispersed in a matrix. In this manner, the novel material structures that are created are characterized by their enhanced mechanical behavior due to the desirable mechanical properties of CNT. However, despite continuous efforts to improve the fabrication procedures used to produce NC, there still exist two important problems that hinder the application of this new kind of material in systems and structures. The first
problem refers to the insufficient knowledge about the reinforcement role of CNT in nanomaterials, taking into account their theoretically remarkable mechanical properties. The second problem refers to uncertainties about the structure of NC due to inherent difficulties in achieving homogeneous dispersions of CNT. In this context, the dissertation introduces a novel multiscale stochastic finite elements method (MSFEM) which models the uncertainties in the structure of polymer nanocomposites (PNC) that comprise polymer matrices and single-walled carbon nanotubes (SWCNT). Furthermore, the method yields values for the mechanical properties of PNC which agree with pertinent experimental findings, and demonstrate the reinforcement capabilities of SWCNT.

The combination of the remarkable mechanical properties of SWCNT and the low density of polymers results in a new kind of composite material that has already been applied in the aerospace industry. In PNC, the incorporation of SWCNT in polymers creates the need to examine the mechanical behavior of PNC at length scales that span the range from the quantum to the macro level because phenomena that occur at small length scales affect corresponding ones at higher scales. This broad range of important dimensions, though, makes PNC modeling a challenging task. Consequently, multiscale approaches have been suggested in the literature to bridge the gap among different length scales and to manage to accurately and reliably model the mechanical behavior of PNC. However, the exact description of the structure and the analysis of the mechanisms that are critical for the mechanical behavior of PNC is difficult. This is due to the importance of atomic interactions, as well as to the influence of processes and laws, such as the quantum theory, which
cannot be readily combined with the existing theory of mechanics of materials. Therefore, approximations and assumptions are made to formulate models which can predict, with varying degrees of accuracy, the response of PNC to given loading conditions. Consequently, such simplifications in the exact atomic and electronic structure of solids lead to discrepancies between modeling and experimental findings. Specifically, computed or measured estimates of fundamental material properties, such as the Young's modulus and tensile strength of nanomaterials, reflect uncertainty which needs to be quantified so that the reinforcing role of NC can be evaluated. This dissertation introduces a new multiscale method capable of determining reliably the mechanical properties of PNC based on actual experimental information.

In modeling multiphase media, such as composite materials, it is important to quantify the effect of a number of parameters which characterize the material's structure and affect its mechanical properties. Therefore, in the case of PNC one wants to know the relative concentration of SWCNT in polymers, as well as the SWCNT size, shape and orientation after mixing. Furthermore, it is important to have reliable estimates of the mechanical properties of SWCNT. This dissertation shows that based on the experimental characterization methods used to assess the quality of the mixing process in PNC fabrication procedures, none of the aforementioned parameters is precisely known or can be accurately computed. Hence, most experimental and modeling findings involve implicitly or explicitly, a number of assumptions and approximations for computing values for important parameters that are needed to determine the mechanical properties of PNC. Thus, the values reported in the
literature are perhaps indicative of the reinforcement capabilities of SWCNT, but they do not provide an accurate description of the mechanical behavior of PNC. In fact, experimental measurements show that many modeling results overestimate the actual mechanical properties of PNC.

The proposed method succeeds in determining the mechanical properties of PNC by using a multiscale approach which relies on observations of the actual structure of PNC at the nano-/microscales. Specifically, the MSFEM presented in the dissertation suggests that depending on the scale of observations, the PNC structure reveals a number of SWCNT formations which have various sizes, shapes, and orientations in the matrix. These formations are randomly dispersed in the material volume and, consequently, they create a kind of spatial randomness in the nano-/microstructure. Hence, the method models PNC as random heterogeneous materials and determines their mechanical properties by incorporating the effect of local material randomness in the bulk behavior.

To derive reliable estimates of important mechanical properties of PNC, the proposed method uses a number of models in a hierarchical multiscale scheme which conveys information from the nano to micro and from the micro to meso/macro scales. This separation of scales approach is necessary since different phenomena occur at different length scales. Therefore, the proposed method shows that the assumption of uniform/homogeneous dispersion is often an idealization of a much more complicated material structure. Specifically, it is shown that variations in the dispersion of SWCNT in polymers cause, at a local level, variations of the local mechanical properties of PNC. This local information is sub-
sequently used to model the effect of the spatial randomness on the overall mechanical properties of PNC. Pertinent assumptions are made based on experimental characterization evidence, and the derived results are compared with corresponding experimental findings which include data from two different kinds of mechanical testing of PNC.

1.2 Outline

This dissertation introduces a novel multiscale method for modeling the mechanical behavior of nanomaterials. Therefore, Chapter 2 provides necessary background by defining the term “nanotechnology” and by stressing the importance of the length scale in phenomena that occur at the atomic and subatomic levels. Chapter 2 is essentially an engineering perspective on nanotechnology, and, therefore, the goals and applications described in this chapter focus on the mechanical reinforcement role of nanomaterials. Hence, novel materials, such as the CNT, are described in this chapter as a new kind of structural material which can be used in macroscopic engineering applications. CNT are the important component in the PNC modeled in this dissertation because of their mechanical properties. Therefore, Chapter 2 explains how the mechanical behavior of CNT is related to their atomic and electronic structure, as well as to the fabrication methods and post-fabrication procedures used to produce them. This information is further used in subsequent chapters to support choices in values for parameters which affect the results computed by the proposed method. Additionally, a review of the experimental, the analytical, and the computational methods used to determine the mechanical properties of CNT are described in Chapter 2 to show that the
suggested values in the literature present significant variations. Such variations increase the uncertainty related to the actual reinforcing capabilities of CNT, and create the need for reliable modeling of CNT and CNT-reinforced composites.

Chapter 3 focuses on PNC production, characterization, and modeling. Hence, this chapter begins with a description of the polymer’s chemical structure which is later used in the proposed method to support the choice of the values of parameters that affect the mechanical properties of PNC. Further, Chapter 3 describes the experimental procedures used to mix polymers with SWCNT to produce novel PNC. The difficulties in the fabrication procedures are treated in this chapter as sources of uncertainty that are subsequently quantified to fully harness the potential of SWCNT as reinforcement agents. The critical role of the load transfer between the matrix and the SWCNT in PNC is also discussed in Chapter 3 to point out the problems encountered in the case that SWCNT are used to enhance the mechanical behavior of other materials. The reinforcement role of SWCNT also depends on the size, shape, and orientation distribution of nano-/microscale formations in polymers which are further randomly dispersed. Consequently, Chapter 3 identifies critical parameters pertinent to the PNC structure that need to be quantified to effectively model the mechanical properties of PNC. Furthermore, this chapter describes experimental testing procedures used to characterize the mechanical properties of PNC. Findings of two of these testing procedures are incorporated in the proposed method to model realistically the structure of PNC, and to determine reliably their mechanical properties. Chapter 3 concludes with a review and evaluation of the various kinds of models that have been suggested in the
literature to model the mechanical behavior of PNC. These models include the so-called multiscale methods which incorporate computational and analytical components that are used to model various aspects of the PNC structure and mechanical behavior at different length scales. The advantages and disadvantages of each method are analyzed and a number of the assumptions and findings described are found useful to the goals of this dissertation, and are thus incorporated in the proposed method presented in Chapter 4.

The proposed multiscale stochastic finite elements method (MSFEM) used in this dissertation for determining the mechanical properties of PNC is developed in Chapter 4. Specifically, this chapter explains the reasons why PNC should be treated and modeled as random heterogeneous media. Therefore, the structure of PNC is represented using a number of models in a hierarchical scheme that uses information obtained at the nano and micro scales. The proposed MSFEM identifies a specific material region (MR) with finite dimensions as representative of the overall bulk material. In this MR, the dispersion of SWCNT in polymers is modeled and quantified using the SWCNT volume fraction (VF) as a descriptor which shows the relative concentration of SWCNT at a local level. The local SWCNT VF is represented by a random field model that is capable of capturing the spatial randomness in the structure of PNC. Therefore, randomness is induced in PNC by the non-homogeneous dispersion of SWCNT in polymers. The developed random field model includes parameters that can be adjusted according to experimental information relevant to the dispersion properties of SWCNT in PNC, obtained by imaging and characterization methods. The random field model is also used in the proposed MSFEM to formulate a
finite element (FE) scheme which is used to determine the mechanical properties of PNC. Furthermore, the proposed method models PNC as a two-phase material; it further quantifies the number of SWCNT which are either homogeneously dispersed in the matrix or agglomerated in the form of spherical inclusions. In addition, the method determines the mechanical properties of the PNC at a local level by a micromechanics homogenization approach. These local properties are subsequently used in the FE scheme which yields estimates for the effective mechanical properties of PNC using a Monte Carlo simulation technique.

The proposed method, as described in Chapter 4, is applied in Chapter 5 to determine the Young's modulus (YM) and Poisson ratio (PR) of PNC. Specifically, pertinent experimental characterization information is presented, and it is used to select values of various material parameters in the proposed MSFEM. Two particular PNC are selected for modeling purposes, due to the fact that sufficient information has been reported in the literature regarding their structure, and experimentally measured properties. The application of the proposed method shows that it succeeds in providing estimates for the YM and PR of PNC which agree with pertinent experimental findings in the literature. Consequently, the MSFEM shows that the effect of spatial randomness in the structure of PNC is an important parameter that should be taken into account in characterization and modeling of the mechanical properties of PNC. It is further shown that the direct use of analytical methods is not always appropriate for modeling of PNC because of important information which is either averaged or ignored. The proposed method presents a more realistic approach
in modeling of nanomaterials and focuses on an aspect of the PNC structure, the spatial randomness, which has not been yet reported in the literature.

An additional application of the proposed method is presented in Chapter 6 in modeling experimentally obtained nanoindentation (NI) data. NI testing results are treated in this chapter as information regarding the local YM of PNC. Consequently, the proposed method is used to incorporate this local information in a modeling scheme capable of determining the overall mechanical properties of PNC. To this aim, the variations observed in NI measurements are used to define an appropriate random field model which represents the spatial randomness in PNC induced by the non-uniform dispersion of SWCNT in polymers. The proposed method generates numerical NI data which represent different dispersion cases. The simulated data are subsequently used in a FE method to determine the overall YM of PNC by solving a specific elasticity problem instead of simply averaging values, as is currently reported in the literature. Thus, the MSFEM yields YM values which agree with pertinent experimental findings, while they are more reliable than corresponding results that could be obtained by direct averaging of NI data. Hence, a practical modeling strategy is formulated, and it can be applied to reliably determine the YM of PNC based on NI data.

Chapter 7 presents one more application of the MSFEM. Specifically, the elastic instability or buckling of PNC structures is investigated to determine the effect of the incorporation of SWCNT in polymers. Thus, Chapter 7 derives the governing equation of buckling of thin plates. This equation is solved analytically and numerically by using specific sets
of boundary conditions. The numerical model used to study the elastic instability of PNC structures is developed in the ANSYS software, and it is further used to compute the buckling loads and modes of the two polymers and the corresponding PNC described in Chapter 5. The computed results show that the buckling loads are higher in the case of the PNC, due to their higher YM compared to the polymers. Moreover, a Monte Carlo model also developed in ANSYS is used to validate the use of the effective mechanical properties of PNC computed in Chapter 5, in modeling the buckling behavior of PNC structures with random mechanical properties. The agreement between the Monte Carlo results and the ones obtained by using the effective values shows that the estimates for the YM and PR computed by the MSFEM can be reliably used for modeling of the mechanical behavior of PNC at the micro-/meso-/ and macroscales.

In summary, the dissertation introduces a novel multiscale method for determining the mechanical properties of PNC using information obtained by experimental characterization and testing methods. The method points out that the effect of spatial randomness in the structure of PNC is an important parameter that should be taken into account in modeling and characterization of PNC. In this context, a procedure is developed to use information obtained at the nanoscale in models that are defined at the microscale and are capable of providing estimates for the mechanical properties of PNC at the macroscale. This bridging of scales is supported by appropriate assumptions which take into consideration specific experimental information. Thus, the dissertation contributes to understanding the reinforcement capabilities of SWCNT, and succeeds in combining information, at var-
ious scales, that affects the mechanical behavior of PNC.
Chapter 2

Nanotechnology: An Engineering Perspective

This chapter presents an introduction to nanotechnology from an engineering point of view. A definition of the term “nanotechnology”, its goals and applications, as well as a brief historical background are provided with a particular emphasis given to carbon nanotubes (CNT) because of their role in this dissertation. In this context, this chapter analyzes the CNT structure and cites the most important production and post-fabrication treatment methods. In addition, Chapter 2 focuses on the mechanical properties of CNT and the various methods currently used to measure them.
2.1 Definition

The term “nanotechnology” is used to refer to technology on the order of nanometers (nm). A nanometer is equal to a billionth of a meter and, at this scale, matter behaves in a different manner compared to what is experienced in everyday life. Figure 2.1 presents a scale of things in nature and the sizes of certain characteristic objects. An interesting example that shows the length scale of interest in nanotechnology, is the comparison of one nanometer with the diameter of a human hair; Figure 2.1 shows that this diameter is approximately 60-120 \( \mu m \), which means that a human hair is 60 to 120 thousand times bigger than the diameter of a carbon nanotube.

The number of scientific areas that are related to nanotechnology is large, and despite the use of the prefix “nano”, there is often ambiguity as to what is really called nanotechnology. In brief, many technical definitions exist depending on the viewpoint adopted. A suitable definition that stresses the interdisciplinary nature of nanotechnology is provided by the National Nanotechnology Initiative (NNI)(http://www.nano.gov). According to NNI Nanotechnology is:

i) research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1-100 nm range.

ii) creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.

iii) ability to control or manipulate on the atomic scale.
2.2 Goals and applications

The effect of nanotechnology on everyday living is already significant and, thus, there exists increasing interest in the subject. Working at the nanometer range means that the frontier of atoms is reached. Nature is composed of atoms, and thus, the ability to manipulate matter at the atomic level offers new ways to better understand the materials world. Moreover, the basis of life, DNA, has dimensions on the order of a few nanometers and the investigation
of the phenomena that occur at this scale can result in improvement of human life. Hence, nanotechnology offers a new route for scientists to explore and explain the core of this world.

The way atoms in nature group to form molecules and larger systems determines the chemical, physical, mechanical and other known material properties. Understanding how nature works at this level is advantageous to the control and design of better "things." Therefore, the goal in nanotechnology is to create stronger, "smarter," multifunctional, cheaper, less harmful and friendlier to the environment applications following one of two approaches. The first, termed "top-down," refers to the design of objects starting from the macroscale and gradually moving toward their structure in lower dimensions. An example of this approach is the chips used in integrated circuits of modern computers. The second approach, called "bottom-up," includes any procedure which starts from, e.g. the level of atoms, and by appropriate techniques manages to group functions and systems to something that is orders of magnitude larger. An example of this case is novel nanocomposite materials, such as the ones examined in this dissertation, in which the structure at the nanoscale affects the macroscopic material properties.

A significant number of nanotechnology applications can be found in many scientific areas. In particular, nanoelectronics applications have been developed that will result in the next generation of computers. Today's commercial integrated circuits have characteristic dimensions of the order of micrometers and, because of their size, they have an upper limit to their capabilities, such as storage space and computational power. The advent of
nanotechnology has resulted in new circuit components that are thousands of times smaller compared to the ones currently used. For example, carbon nanotube field-effect transistors [64] and single-electron transistors [4] have already been tested and implemented. Furthermore, nanotechnology has a significant impact on the area of telecommunications. Specifically, nanophotonics applications have been used in fiber optics cables to transmit information faster and without losses [46]. In addition, the role of nanotechnology in energy is very important. Energy transfers can be assisted by using "nanowires," also called "quantumwires," that have similar or better conductivity than existing ones made of aluminum, yet weigh less [116]. In the case that a "nanowire" is made of a specific kind of CNT, then, theoretically, electron transfer could take place in a ballistic way which would minimize any losses. Moreover, CNT have been used in solar cells to produce a pollution-free and infinitely renewable source of energy [88]. Also, nanotechnology applications have been developed for the production and storage of hydrogen, a very promising alternative fuel [12].

Finally, within the scope of this dissertation the mechanical engineering applications of nanotechnology are discussed. Specifically, it is pointed out that the exceptional mechanical, electrical, thermal and other properties of novel nanomaterials have attracted the interest of scientists and engineers. For example, the role of nanomaterials in enhancing the mechanical behavior of engineering structures is demonstrated by the idea of the space elevator. A space elevator is essentially a long cable extending from Earth's surface into space with its center of mass at geostationary Earth orbit. Electromagnetic vehicles trav-
eling along the cable could serve as a mass transportation system for moving people, payloads, and power between Earth and space. Obviously, the material properties required to make this plan feasible are extreme. CNT appear to have theoretically the required strength which, under the appropriate conditions, could lead to the development of a structure similar to a space elevator [19].

2.3 Historical background

Nanotechnology is not a new and self-inclusive science. On the contrary, it is a vast interdisciplinary area that has existed for centuries. For example, the stained-glass windows found in medieval churches have a variety of colors due to gold nanoparticles of different sizes that were included in the glass [9]. However, due to the length scales involved in nanotechnology applications, it was not until the invention of certain types of electron microscopes in the 1980s, capable of achieving resolutions on the order of atomic dimensions, that systematic versus empirical development in this field could be achieved [115]. Indeed, the advent of potent imaging techniques capable of viewing and manipulating nano-sized particles, such as the scanning electron microscope (SEM), the scanning tunneling microscope (STM) and the atomic force microscope (AFM), shed light on objects that were almost out-of-sight and stimulated the interest of scientists for research in the realm of atoms. Although, physics and chemistry at the atomic and subatomic level had been known since the beginning of the 20th century and had been well-described in the quantum mechanics theory, it took decades to develop the appropriate tools to verify these theoretical predictions.
Obviously, the growth of nanotechnology has always depended on advances in technological equipment.

Besides the technological advances that have helped the development of nanotechnology, two scientific discoveries gave this field a tremendous “boost”. The first occurred in 1985, when scientists at Rice University discovered the fullerenes, or buckminsterfullerenes, or \( C_{60} \) (carbon-sixty), also known as buckyballs (Figure 2.2). The importance of buckyballs for chemistry and the new perspectives that they offered became obvious when Professors Smalley and Curl from Rice University and Professor Kroto from the University of Sussex (UK) were awarded the 1996 Nobel Prize in chemistry. Their discovery proved that theoretical predictions were correct. Furthermore, carbon was involved and the dimensions of the discovery were on the order of nanometers. Carbon is a dominant element in nature and the existence of a new structure or allotrope as it is referred to in chemistry [89], generated immediate hopes for “nano”-type applications.

Buckyballs are spherical molecules consisting of sixty carbon atoms. Their diameters are on the order of approximately 1 nm. Their importance stems, first of all, from their existence and, further, from their structural properties. Based on a theorem by Euler, sixty carbon atoms form a unique stable structure if and only if they form exactly twelve pentagons and twenty hexagons. Nevertheless, bigger fullerenes containing seventy and eighty carbon atoms exist. Further, because of their size and structure, buckyballs have been used in a number of applications. For example, it has been shown that buckyballs act as antioxidants and, therefore, they can be used to neutralize free radicals that exist in the human
Figure 2.2: The two widely known allotropes of carbon, diamond and graphite, and the recently discovered third one called $C_{60}$ (carbon-sixty). A single-wall nanotube is a structure with nanoscale dimensions that can be thought of as the combination of graphite and $C_{60}$ molecules.

body [30]. Moreover, buckyballs have been used as contrast agents in medical imaging instrumentations [98] as well to deliver drugs [110].

The next most important discovery in the area of nanotechnology was that of CNT in 1991 by Iijima [42]. The mechanical, electrical, physical and thermal properties of this material make it unique. These "nanotubes" are the stiffest and toughest material ever known, they conduct electricity better, theoretically, than any other material and their thermal conductivity is twice that of diamond. Their diameters are on the order of nanometers, and
their density is relatively low (see section 2.4). Furthermore, this material can be used as the reinforcement component in composite structures. In fact, the reinforcement function of CNT in novel polymer nanocomposite materials is modeled in this dissertation. The structure and properties of CNT are presented next.

2.4 Carbon Nanotubes

The discovery of CNT by Iijima [42], resulted in an impressive research effort in the area of nanotechnology. For engineering applications, the supreme mechanical properties of CNT are needed to enhance the macroscopic response of materials to mechanical loads. Such properties include the tensile modulus and strength, the elongation prior to fracture and the large aspect ratios. The advent of CNT, resulted in the design of novel structures known as nanocomposites (NC). In NC, common materials, e.g. polymers, ceramics, metals, etc., are reinforced with CNT. In this manner, the mechanical behavior of NC is enhanced even for small CNT volume fractions [72].

Due to the nanoscale dimensions of CNT, it is very difficult to measure their mechanical properties. Therefore, a number of specialized experimental techniques as well as group of analytical and computational methods have been developed to estimate the “true” mechanical properties of CNT at the nanoscale. These techniques and methods are presented in this chapter, since they are related to the need to characterize reliably the properties of PNC and ensure their successful implementation in real-world applications.
2.4.1 Structure

Carbon nanotubes can be thought of as graphene sheets rolled into cylinders as presented in Figure 2.3 [89]. The rolling occurs in the direction defined by a "chiral" vector \( r \) or equivalently by the "chiral" angle \( \theta \).

![Diagram of graphene sheet and nanotube structure](image)

Figure 2.3: Schematic representation of the unrolled structure of CNT. Rolling in the direction of the chiral vector \( r \) or according to the chiral angle \( \theta \) results in the formation of the nanotube. The chiral vector is defined by the unit vectors \( \alpha \) and \( b \).

The chiral vector is defined in Equation 2.1

\[
\mathbf{r} = n\mathbf{\alpha} + m\mathbf{b}
\]  \hspace{1cm} (2.1)

where \( n \) and \( m \) are integers and \( \mathbf{\alpha} \) and \( \mathbf{b} \) are unit vectors which for the hexagonal lattice of carbon atoms in the graphene sheet are defined in the real space as

\[
\mathbf{\alpha} = \left( \frac{\sqrt{3}}{2}a, \frac{a}{2} \right)
\]  \hspace{1cm} (2.2)

\[
\mathbf{b} = \left( \frac{\sqrt{3}}{2}a, -\frac{a}{2} \right)
\]  \hspace{1cm} (2.3)
The parameter $a$ is defined in Equation 2.4

$$a = |\alpha| = |b| = b_c \sqrt{3} \text{ in } \text{Å}$$  \hspace{1cm} (2.4)$$

where $b_c$ is the bond length between two carbon atoms of the CNT, equal to 0.142 nm.

Furthermore, based on Figure 2.3, the chiral angle $\theta$ of CNT can be found by using Equation 2.5.

$$\theta = \cos^{-1} \frac{r \cdot \alpha}{|r||\alpha|}$$  \hspace{1cm} (2.5)$$

In addition, the diameter of the CNT is found by using Equation 2.6

$$d = \frac{L}{\pi} = \frac{|r|}{\pi} = \frac{a\sqrt{n^2 + m^2 + nm}}{\pi} \text{ in } \text{Å}. \hspace{1cm} (2.6)$$

In Equation 2.6, $L$ is the circumference of the CNT. The density of the CNT is defined in Equation 2.7 [82].

$$\rho = \frac{4NM_w}{\pi N_A d^2}$$ \hspace{1cm} (2.7)$$

where $d$ is the diameter of the CNT, $M_w$ is the atomic weight of carbon, $N_A$ is Avogadro’s number, and $N$ is used to express the number of carbon atoms per unit length and is equal to

$$N = \frac{4\sqrt{n^2 + nm + m^2}}{3b_c}. \hspace{1cm} (2.8)$$

Based on the values of $n$ and $m$ in Equation 2.1 or equivalently on the value of the chiral angle $\theta$, three types of CNT can be defined:

$$\theta = 30^\circ \text{ or } n = m \text{ Armchair} \hspace{1cm} (2.9)$$

$$\theta = 0^\circ \text{ or } m = 0 \text{ Zigzag} \hspace{1cm} (2.10)$$

$$0 < \theta < 30^\circ \text{ or } n \neq m \text{ Chiral.} \hspace{1cm} (2.11)$$
Figure 2.4 presents these three types of CNT and provides an illustration of their ends which typically consist of hemispheres of fullerenes that are selected to fit the circular cross-section. The three types of CNT have in general different mechanical, electrical and other properties due to the position of carbon atoms on the sidewall.

![Examples of the three types of carbon nanotubes based on their chiral vector and the corresponding “caps” used to close their ends](image)

**Figure 2.4:** Examples of the three types of carbon nanotubes based on their chiral vector and the corresponding “caps” used to close their ends [84].

The CNT walls could consist of one, two or more concentric layers of carbon atoms held together by electrostatic forces. The interlayer spacing between the walls is approximately 0.34 nm, which is very close to the interlayer separation between parallel layers of graphite. Figure 2.5 presents the first nanotubes reported by Iijima [42] which were multi-walled carbon nanotubes (MWCNT) consisting of several layers. However, it has been reported that the mechanical properties of single-walled carbon nanotubes (SWCNT) are better compared to the ones of MWCNT and thus, more attention has been given to SWCNT, especially for material reinforcement purposes, as presented in this dissertation.
2.4.2 Production methods

The successful incorporation of CNT in real-world applications depends on the ability to produce large quantities of high quality nanotubes. Currently, several experimental methods are used by various research laboratories and companies around the world to produce this kind of nanomaterial. The particular production method followed affects both the quantity and the quality of the resulting nanotubes. Consequently, the mechanical and other properties of CNT present significant variations, as shown in this chapter. Therefore, it is important to take into consideration the role of the production methods in subsequent stages of design and modeling of materials and systems, as pointed out in this dissertation. Next, five of the most used methods to produce CNT are presented.
High-pressure carbon monoxide deposition (HiPCO)

High-pressure carbon monoxide deposition (HiPCO) has been developed at Rice University and is the first continuous flow process suitable for large scale production of high-quality nanotubes [87]. HiPCO involves a high-pressure heated reaction chamber, through which there is a flow of carbon monoxide gas mixed with industrial gas that contains the necessary catalysts to sustain the chemical reactions required to create nanotubes. The catalysts consist of iron atoms and assist the carbon monoxide molecules to break up into carbon and oxygen atoms. The resulting carbon atoms form the lattice structure of CNT. The remaining oxygen atoms join the available, in the chamber, carbon monoxide molecules to form carbon dioxide. The temperature and pressure conditions required in the HiPCO method are common in industrial settings, a fact that makes its implementation relatively low-cost [89]. CNT produced by the HiPCO method constitute the reinforcement phase of one of the two particular nanocomposites modeled in this dissertation.

Arc discharge

The carbon arc discharge method is the most widely used method to produce large quantities of CNT at low-cost due to its relatively simple procedure [96]. Specifically, nanotubes are created through arc-vaporization of two carbon rods placed end to end in a chamber that contains an inert gas under low pressure conditions. The application of a direct current creates a high temperature discharge between the two electrodes. This process vaporizes one of the carbon rods and results in a deposit on the other. A disadvantage of the arc discharge method is that it usually produces a variety of nanotubes which can be separated only after
applying post-processing techniques. CNT produced by the arc discharge method are used as reinforcements in a particular nanocomposite modeled in this dissertation.

Laser vaporization

The laser vaporization method, used to synthesize bundles of SWCNT, is based on two sequenced laser pulses on a graphite target under high temperatures and in an inert gas environment. The use of two successive pulses minimizes the amount of graphite that does not participate in the formation of nanotubes. The outcome of this method is a form of CNT bundles with varying diameters. By varying the temperature and other growth parameters, the quality of the produced nanotubes can be partially controlled. This is an advantage of laser vaporisation method compared to the arc discharge.

Chemical-vapor deposition (CVD)

An effective method to produce CNT is the chemical vapor deposition (CVD) [115]. This method uses a carbon source (methane gas, carbon monoxide, acetylene etc.) in a heated chamber, over a catalyst which is coated by a substrate. The catalyst is usually a metal such as nickel, iron or cobalt. The temperature in the chamber is high enough to break the molecules of the carbon source and to produce free carbon atoms. Subsequently, CNT are formed if the proper parameters are maintained. This technique has advantages over the laser and arc discharge methods described previously because it does not vaporize carbon. Therefore, it succeeds in reducing the unwanted mixtures of CNT with other substances and results in less entanglement.
**Vapor growth**

Vapor growth methods utilize procedures similar to the fabrication of vapor-grown carbon fibers [89]. In vapor growth, various carbon sources have been used in the presence of iron particles to form CNT. A significant advantage of the method is that it can be used for continuous fabrication of CNT, if appropriate conditions are satisfied. A disadvantage of the vapor growth is that it produces multi-walled CNT which usually contain regions where carbon is still amorphous. Thus, the properties of the CNT obtained by vapor growth are worse compared to the ones measured from CNT produced by other methods.

### 2.4.3 Post-fabrication treatment

In practice, no production method has resulted in “perfect” CNT. This perfect type of nanotubes would have no impurities such as foreign atoms or defects in their structure. Unfortunately, the characterization processes used to assess the quality of the nanotubes as received after the fabrication stage show that currently there are always some impurities and defects which are in most cases associated with the catalyst or the substrate used. For this reason, a number of post-fabrication methods have been suggested to improve the quality of CNT, and they are presented next.

**Purification**

The presence of impurities in CNT after the fabrication stage, such as unwanted non-carbon or amorphous carbon atoms, affects their material properties. In addition, MWCNT need to be separated from SWCNT. These tasks are performed, with a varying degree of
success, in the purification stage. Common ways to purify the "as-received" CNT include strong oxidation followed by an acid treatment. This oxidation process has proved to be an effective way to remove non-carbon atoms from nanotubes. However, it is also true that during oxidation, the nanotubes could be damaged. Therefore, alternative methods, such as the scalable multi-step purification method proposed by Xu et al. [120], have been used to avoid damage on CNT. Additional purification methods include the use of organic polymers that are capable of interacting with specific tube diameters, thereby separating them from amorphous carbon [37]. Finally, filtering [94], size exclusion chromatography [17] and ultrasonication in the presence of surfactants [56] have been applied for the purification of MWCNT and SWCNT.

**Functionalization**

The incorporation of CNT into other structures is hindered by the smooth and non-reactive surface of the nanotubes. Specifically, CNT adhere poorly to other materials. The lack of interfacial bonding between CNT and other materials affects the load transfer from the weak phases to CNT. Experimental evidence proves that CNT are pulled out from the matrices, and therefore, their reinforcement role becomes limited. Furthermore, CNT in composites are usually bundled in the form of ropes and agglomerates (see Chapter 3).

The CNT-matrix interface properties and the un-roping of CNT bundles can be improved by using functionalization processes. In functionalization, various atoms and molecules are bonded to the surface of CNT in multiple sites. Generally, there are two methods to functionalize CNT: covalent and non-covalent. A common covalent functionaliza-
tion method consists of direct fluorination and addition of amines and acyl peroxides [48]. However, it has also been reported that covalent functionalization could have a negative impact on the properties of CNT because it chemically modifies the sidewalls affecting their mechanical and electrical properties [117]. Therefore, non-covalent functionalization efforts have also been suggested [86, 117]. In non-covalent functionalization, the molecules used to achieve better dispersion and improve the interfacial strength interact without being bonded with the sidewalls of the CNT.

2.4.4 Mechanical Properties

The mechanical properties of materials depend on their atomic structures and interactions [47]. Each atom comprises a number of electrons that move around the nucleus following certain paths, called orbitals. These atomic orbitals are not arbitrary. In fact, there is a set of four quantum numbers (QN) that describe the electron quantum states, i.e. the available orbitals for each electron. Based on the Pauli exclusion principle, no two electrons have all four QN the same. Each QN describes certain characteristics of the atomic orbitals. Specifically, the first is called primary QN and designates the size of the orbital and its energy level. The energy levels increase as the distance of the electrons from the nucleus becomes larger. In an atom the electrons that have the same primary QN belong to the same shell. Each shell is composed of sub-shells that have the same second QN called angular QN. This QN is usually denoted with letters such as $s, p, d, f$, etc. corresponding to a particular shape of an orbital; for example, $s$ denotes spherical. The third and fourth QN
are called magnetic and spin QN and denote the energy levels available for each electron in the sub-shell and the intrinsic or spin angular momentum of the electrons respectively.

The electronic structure of atoms previously described is provided by Quantum Mechanics (QM). In QM, the solution of equations such as the Schrödinger wave equation is used to compute the QN for the electrons in a particular system of atoms. However, although exact solutions exist for some canonical problems, in most cases only approximate solutions can be found [47]. Due to the uncertainty principle of Heisenberg, even if the QN of electrons in a single atom are known, their exact location and momentum cannot be determined at the same time. Therefore, atomic orbitals are essentially probability spaces, where electrons are allowed to exist. The combinations between the atomic orbitals result in complicated molecular orbitals that affect the material properties.

The mechanical properties of nanoscale materials depend heavily, because of their dimensions, on the quantum mechanical description of their electronic structure. In the case of carbon-based nanomaterials, the chemical properties of carbon play also an important role. Carbon is a dominant element in nature because of its atomic structure. Its atomic number is equal to six and, therefore, six electrons exist in each atom. Two of these electrons belong to the first energy level, which has a spherical shape; the remaining four belong to the second energy level and are the valence electrons since they belong to the last available shell. Two sub-shells, one of s and the other of p type, with two electron each are available in the outer shell of carbon atoms. Thus, the electronic structure of a carbon atom is $1s^22s^22p^2$. 
Since carbon atoms have four valence electrons they can form up to four bonds with other atoms. In CNT, the atoms are arranged in the hexagonal structure of a benzene ring as illustrated in Figure 2.6. The bonds between carbon atoms are formed by electron interactions between neighboring atoms. In addition, atomic orbitals in CNT form new molecular orbitals when combined.

![Diagram](image)

Figure 2.6: Basic hexagonal (benzene) structure of graphite. The carbon nuclei which are represented by the filled dots are connected with the in-plane σ-bonds while the remaining electrons form out-of-plane π-bonds [84].

Specifically, one of the s-valence electrons of one atom is combined with two p-electrons of another atom to form three new hybrid orbitals at an angle of 120° with respect to each other. The hybridization that occurs in this way is called $sp^2$ and is graphically presented in Figure 2.7. This type of hybridization occurs also in graphite and is the strongest among those similarly formed between any atoms of the periodic table. The $sp^2$-bonds belong to the same plane; the remainder s-valence electron of each atom, that did not participate in this hybridization, follows an orbital perpendicular to this plane. In the case of the hexagonal ring presented in Figure 2.6, the σ-bonds are in-plane $sp^2$-type bonds that contribute
to the exceptionally high stiffness and strength of CNT. The remaining $\pi$-orbitals are single electrons which are responsible for the good electronic properties of CNT, as well as for the interlayer interaction between neighboring CNT [84]. This electronic interaction is described by Van der Waal (VdW) forces and is much weaker compared to the $\sigma$-bonds. VdW forces also describe the interlayer interaction in MWCNT and are responsible for the inferior mechanical properties of MWCNT.

![Image of sp$^2$ hybridization](http://www.wellesley.edu/Chemistry/chem120/hybrids.html)

Figure 2.7: A schematic representation of the $sp^2$ hybridization. (Figure found in http://www.wellesley.edu/Chemistry/chem120/hybrids.html and modified)

Furthermore, the length of the carbon-carbon bonds in CNT is an additional parameter responsible for their exceptional mechanical properties. Specifically, the bond length in the case of the $sp^2$-hybrid bonds is equal to 0.142 nm and, therefore, is smaller than the corresponding length in diamond (0.154 nm). The smaller bond length practically indicates higher bond strength in the $sp^2$ bonds.

In addition, the fewer defects in CNT compared to other materials contribute to their mechanical behavior. CNT due to their nanoscale dimensions contain fewer defects, such as foreign atoms, missing and hybrid bonds. Consequently, CNT are often considered to be
essentially defect-free materials. This assumption is adopted in theoretical computations to explain the exceptional mechanical properties of CNT. However, the assumption of defect-free CNT leads in discrepancies between experimental and modeling results. For example, in the case of nanocomposite materials in which CNT are dispersed in a matrix, the actual reinforcement capabilities of the CNT are not exactly known. This discrepancy reflects uncertainty in the actual mechanical properties of CNT, as shown in section 2.4.5.

2.4.5 Measurements of the mechanical properties

The mechanical properties of materials are quantified by using certain moduli and constants that describe, for example, their stiffness and strength. Tables 2.1 and 2.2 present the Young’s modulus, tensile strength and density of traditional engineering materials and fibers used in composites. In the case of SWCNT, the values suggested in the literature for their stiffness and strength are obtained by using experimental, analytical and computational methods and are presented in Table 2.3.

Specifically, Table 2.3 presents a representative collection of values for the basic mechanical properties of SWCNT. Based on this information, it can be concluded that SWCNT have better mechanical properties than the materials presented in tables 2.1 and 2.2. In addition, an average value for their density is only 1.44 g/cm³. Consequently, SWCNT have a great potential in enhancing the mechanical properties of advanced composites. However, the values presented in Table 2.3 present significant variations. Thus, Table 2.4 provides the mean value and coefficient of variation of the data presented in Table 2.3. Based on
Table 2.1: Basic mechanical properties of common engineering materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (GPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>0.34-1.9</td>
<td>190-210</td>
<td>7.85</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>0.8</td>
<td>196</td>
<td>7.8</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.07</td>
<td>70</td>
<td>2.71</td>
</tr>
<tr>
<td>Copper</td>
<td>0.23-0.38</td>
<td>110-120</td>
<td>8.94</td>
</tr>
<tr>
<td>Glass</td>
<td>0.03-1</td>
<td>48-83</td>
<td>2.4-2.8</td>
</tr>
<tr>
<td>Iron (cast)</td>
<td>0.07-0.48</td>
<td>83-170</td>
<td>7.4-7.8</td>
</tr>
<tr>
<td>Iron (wrought)</td>
<td>0.34</td>
<td>190</td>
<td>7.4-7.8</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.5</td>
<td>110-120</td>
<td>4.54</td>
</tr>
</tbody>
</table>

Table 2.2: Basic mechanical properties of common fibers

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (GPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon HS</td>
<td>3.5</td>
<td>160-270</td>
<td>1.8</td>
</tr>
<tr>
<td>Carbon IM</td>
<td>5.3</td>
<td>270-325</td>
<td>1.8</td>
</tr>
<tr>
<td>Aramid HM</td>
<td>3.1</td>
<td>120</td>
<td>1.45</td>
</tr>
<tr>
<td>Glass-S</td>
<td>3.45</td>
<td>86</td>
<td>2.5</td>
</tr>
<tr>
<td>Kevlar</td>
<td>2.76</td>
<td>59-124</td>
<td>1.44</td>
</tr>
</tbody>
</table>
Table 2.3: Basic mechanical properties of SWCNT

<table>
<thead>
<tr>
<th>Young's Modulus (GPa)</th>
<th>Tensile Strength (GPa)</th>
<th>Diameter (nm)</th>
<th>Length (nm)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 ± 0.6</td>
<td>NA</td>
<td>1-1.5</td>
<td>23.4-36.8</td>
<td>Experimental</td>
<td>[51]</td>
</tr>
<tr>
<td>0.067-1.31</td>
<td>NA</td>
<td>3-20</td>
<td>100-370</td>
<td>Experimental</td>
<td>[90]</td>
</tr>
<tr>
<td>0.4-3.7</td>
<td>NA</td>
<td>5.6-24.8</td>
<td>1.17-5.81</td>
<td>Experimental</td>
<td>[105]</td>
</tr>
<tr>
<td>1.25</td>
<td>45 ± 7</td>
<td>1.1-1.4</td>
<td>3.7-4.5</td>
<td>Experimental</td>
<td>[112]</td>
</tr>
<tr>
<td>0.31-1.47</td>
<td>13-52</td>
<td>20-41</td>
<td>NA</td>
<td>Experimental</td>
<td>[122]</td>
</tr>
<tr>
<td>0.69</td>
<td>NA</td>
<td>0.5-2</td>
<td>NA</td>
<td>Analytical</td>
<td>[39]</td>
</tr>
<tr>
<td>0.968-0.9686</td>
<td>NA</td>
<td>0.68-27.1</td>
<td>NA</td>
<td>Analytical</td>
<td>[63]</td>
</tr>
<tr>
<td>0.92 ± 0.005</td>
<td>NA</td>
<td>0.41-2.71</td>
<td>7.26-26.9</td>
<td>Analytical</td>
<td>[67]</td>
</tr>
<tr>
<td>0.39-0.4</td>
<td>77-101</td>
<td>0.62-2.67</td>
<td>NA</td>
<td>Analytical</td>
<td>[101]</td>
</tr>
<tr>
<td>4.70</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Analytical</td>
<td>[106]</td>
</tr>
<tr>
<td>0.9-1.25</td>
<td>92.5-126.2</td>
<td>0.34-2.2</td>
<td>NA</td>
<td>Analytical</td>
<td>[119]</td>
</tr>
<tr>
<td>0.5-13</td>
<td>NA</td>
<td>0.2-2.2</td>
<td>NA</td>
<td>Analytical</td>
<td>[124]</td>
</tr>
<tr>
<td>0.475-0.705</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Analytical</td>
<td>[125]</td>
</tr>
<tr>
<td>0.311</td>
<td>4.92</td>
<td>NA</td>
<td>NA</td>
<td>Computational</td>
<td>[16]</td>
</tr>
<tr>
<td>0.92-1.03</td>
<td>92.5-152.3</td>
<td>0.79-0.81</td>
<td>13.2-15.3</td>
<td>Computational</td>
<td>[43]</td>
</tr>
<tr>
<td>0.72-1.1</td>
<td>88-135</td>
<td>0.68-8</td>
<td>NA</td>
<td>Computational</td>
<td>[68]</td>
</tr>
<tr>
<td>0.4-4.15</td>
<td>1.28 ± 0.59</td>
<td>0.54-7.96</td>
<td>NA</td>
<td>Computational</td>
<td>[92]</td>
</tr>
<tr>
<td>0.67-0.7</td>
<td>220-240</td>
<td>0.69-13.3</td>
<td>NA</td>
<td>Computational</td>
<td>[91]</td>
</tr>
<tr>
<td>0.93 ± 0.0115</td>
<td>NA</td>
<td>0.72</td>
<td>NA</td>
<td>Computational</td>
<td>[114]</td>
</tr>
<tr>
<td>0.85-2.55</td>
<td>59.8-62.9</td>
<td>NA</td>
<td>NA</td>
<td>Computational</td>
<td>[118]</td>
</tr>
<tr>
<td>1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Computational</td>
<td>[121]</td>
</tr>
</tbody>
</table>
Table 2.4: Statistics on the data presented in Table 2.3

<table>
<thead>
<tr>
<th>Property</th>
<th>Mean Value (GPa)</th>
<th>Coefficient of Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>102.59</td>
<td>0.69</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>1434</td>
<td>0.8</td>
</tr>
</tbody>
</table>

This preliminary statistical analysis, it is argued in this dissertation that the use of a set of constant/deterministic values to quantify the basic mechanical properties of SWCNT is conditioned by the quality of the approximation and assumptions made. Therefore, a realistic description of the reinforcement role of SWCNT in composite materials can be achieved only if the uncertainty observed in their mechanical properties is appropriately quantified or modeled. To this aim, proposed methods to experimentally, analytically and computationally estimate the mechanical properties of SWCNT are presented next.

2.4.5.1 Experimental Methods

Mechanical properties of CNT have been measured experimentally using mainly three methods. The first is based on axial loading of CNT using appropriate devices and procedures. In the second one, special probes are used to bend CNT. Finally, the third investigates the vibrational behavior of CNT.

*Axial loading of carbon nanotubes*

Walters et al. [112] axially loaded SWCNT ropes using an atomic force microscope (AFM) in lateral mode to measure their Young's modulus (YM). The SWCNT in these experiments were suspended across a hole, and the AFM tip was used to stretch them. To
compute the YM, the authors modeled the suspended SWCNT with an elastic string. The computed values were found to be lower than existing theoretical ones. This discrepancy was caused by the elasticity assumption that the authors made, as well as by the errors in the experimental procedure.

Furthermore, Yu et al. [122] measured the YM of SWCNT ropes which have the closed-pack configuration shown in Figure 2.8. These ropes were axially loaded by an AFM probe which operated inside a scanning electron microscope (SEM). Figure 2.8 illustrates the experimental procedure for this case. Inherent difficulties related to the experimental procedure and the uncertainty with respect to the exact cross-sectional area of the samples were reported in this article to explain the discrepancies observed between the measured values and existing theoretical ones.

**Bending of carbon nanotubes**

Salvetat et al. [90] also measured the YM of SWCNT ropes. The authors adopted a closed-pack model similar to the one presented in Figure 2.8, in the bending experiment that is schematically presented in Figure 2.9. In this testing procedure, the bending load was applied in the middle of the sample which was supported in its ends in a clamped-beam configuration. The proposed values for the tensile and shear modulus of the tested samples were computed using the vertical deflection. However, the exact cross-section of the samples was not known; a cylindrical one was assumed by the authors. This assumption resulted in errors in the computed values for the mechanical properties.
Figure 2.8: Schematic representation of the technique used to axially load SWCNT ropes (above) and the assumed closed-pack model for the carbon nanotube ropes (below) [122]

Figure 2.9: A method to measure the elastic properties of CNT using an AFM tip to bend a clamped beam configuration [90]
**Vibrations of carbon nanotubes**

Treacy et al. [105] provide estimates for the YM of CNT by measuring the amplitude of their intrinsic thermal vibrations in a transmission electron microscope (TEM). Specifically, the nanotubes were assumed to have a cross-section similar to an annulus with given inner and outer diameters. Subsequently, the vibration amplitude at the tip of a cantilever beam model was associated with its YM. Specifically, the authors obtain values for this material property by equating the vibration energy of the beam with the thermal energy induced by heating. This technique is based on a stochastically loaded beam model which assumes that on the average the vibration profile of the tip follows a particular probability distribution. The same technique was applied by Krishnan et al [51] to model the freestanding room temperature vibrations of SWCNT rods in a TEM.

### 2.4.5.2 Analytical methods

Analytical methods have been proposed as an alternative to the tedious experimental procedures used to measure the mechanical properties of CNT. These methods are based on principles of continuum mechanics, lattice dynamics and crystallography. In general, assumptions are made in analytical methods to overcome difficulties related to the discrete nature of matter at the nanoscale. Therefore, the atomic interactions are usually modeled analytically by using some potential function that, depending on the level of sophistication of each method, is selected to incorporate different aspects of these interactions. Consequently, continuum methods have resulted in models that yield estimates for the mechanical
properties of SWCNT by respecting the physics and chemistry at the nanoscale. Some examples of continuum models are reported next.

Lu et al. [63] compute the bulk, Young’s and shear modulus of SWCNT using empirical lattice dynamics. The atomic interactions in the method presented by these authors are modeled by using pair-wise harmonic potentials which are, further, assumed to be similar to the ones appearing in graphite. The values for the mechanical properties of SWCNT in this article are computed by using the material’s strain energy density and by assuming a value for their thickness. Tu and Yang [106] also used a continuum method to compute the Young’s modulus and Poisson ratio of SWCNT. Their method is based on an expression of the complete energy for a deformed SWCNT which, according to the authors, is consistent with the classical shell theory. The suggested values for the SWCNT mechanical properties, in this article, agree with other modeling results. Furthermore, Zhang and Guo [124] predict the mechanical properties of SWCNT using a modified Cauchy-Born rule (CB) which is based on the assumption that the deformation of the continuum is related to that of the crystal lattice. The authors investigate the effect of the interatomic potential and the CNT thickness and diameter on the SWCNT properties. A similar approach is followed by Guo et al. [39]. Moreover, Zhang et al. [125] develop a continuum model to compute the mechanical properties of SWCNT. This model is used to link the structure of the material at the atomic level with a constitutive formulation. The authors report good agreement between modeling and experimental results.

An interesting class of continuum methods capable of furnishing the mechanical prop-
erties of CNT is known as molecular structural mechanics. These methods use principles from structural analysis in canonical molecular models. For example, Xiao et al. [119] present an analytical molecular structural mechanics model capable of computing the Young's modulus, Poisson ratio and stress-strain relationships of CNT under tension. This model is, according to the authors, much simpler compared to others while it succeeds in computing the nanotube properties. In addition, Sun and Zhao [101] and Meo and Rossi [67] propose molecular-mechanics based finite element (FE) models to compute the mechanical properties of SWCNT. In both models, the atoms are viewed as interacting material points. The type of interaction is defined by a potential function. Although the use of FE in molecules is based on many simplifying assumptions the authors in these two papers claim that molecular structural mechanics is a much simpler alternative to expensive atomistic simulations. Indeed, this method enables the use of computationally less expensive techniques, such as FE, to compute mechanical properties for nanoscale materials. However, critical parameters in molecular structural mechanics, as for example the existence of defects on the sidewall, are ignored and, therefore, there is room for further improvement of the method in the context of modeling of nanomaterials.

2.4.5.3 Computational methods

The task of measuring and estimating experimentally the mechanical properties of CNT is difficult due to the inherent problems related to the length scales involved. The experimental results suggested in the literature are derived based on critical assumptions about the na-
ture of CNT and their mechanical behavior. The continuum assumption is adopted in most cases and the material parameters computed depend strongly on this choice. Consequently, the problems encountered in handling CNT and repeating cumbersome experimental techniques have resulted in the development of computational methods capable of computing properties at the nanoscale. Computational methods are generally classified according to the assumptions and approximations on which they are implicitly or explicitly based. In this context, it should be noted that since CNT have dimensions measured in nanometers, the effects of the electron and atomic interactions on their properties are important. Such interactions are usually neglected or averaged in continuum models. Therefore, computational methods are a valuable source of information about the properties of nanomaterials because they are based either on the exact electronic structure of carbon atoms or make some pertinent assumptions and approximations to incorporate some of the information carried by the electrons.

The main objective of any computational method is to mathematically model the total energy of the system of interest. This energy is a function of the components of the system and it describes the way that the system can evolve in space and time. The minimum of this total energy function at zero temperature represents the static equilibrium of the system. In equilibrium, the forces exerted between the components of the system can be found by differentiation of the total energy function with respect to all the variables that describe the state that the system exists. Knowledge of these forces is necessary to describe the behavior of the system according to laws of mechanics. In the case that the dynamic
behavior of the system is investigated, its evolution in time because of the interactions between its components is needed.

The various ways that have been proposed to compute the total energy of a system that consists of a number of "particles", for example atoms, has resulted in a variety of computational methods. In the case that an explicit dependence of the system's energy on the subatomic structure of the interacting particles is sought, then quantum mechanical computations are necessary. By solving equations like the previously mentioned Schrödinger wave equation, a description of the system's total energy is achieved. However, solving the Schrödinger equation is usually very difficult for systems that consist of many particles. For this reason, a variety of methods called \textit{ab initio} or first-principles have been developed which are capable of providing approximate solutions to this kind of quantum mechanical equations. The most important approximations include the tight-binding, Hartree-Fock and density functional theory methods [60, 74]. \textit{Ab initio} methods have been used by Mielke et al. [68], Sanchez-Portal et al. [92] and Xia et al. to compute the mechanical properties of SWCNT.

The description of the system using first-principles depends on the exact electronic structure of atoms and, therefore, most \textit{ab initio} methods have difficulties in analyzing large systems because of the amount of computations involved. One way to reduce the computational time is by using molecular mechanics methods which are suitable both for static and dynamic problems. In static problems, molecular methods compute the minimum total energy of the structure, while in dynamic ones the evolution of the system in space
and time is computed [28].

In the case that the system of atoms considered is modeled by a set of interacting particles with specific masses, molecular dynamics methods (MD) are used. In MD, for each particle and in every point in time, a vector of the instantaneous position and velocity is needed. Usually, the behavior of a number of particles is modeled in an appropriately defined "window" in which a number of parameters are held constant, such as the total number of atoms, the volume, the temperature, the pressure, the energy and others. The choice of which parameters are fixed affects the positions and velocities of the particles. Additionally, in MD an expression for the equation of motion of the system is formulated. This equation includes the contribution of the kinetic and potential energy of the system. Various approaches can be followed to achieve this goal, such as the Lagrangian or the Hamiltonian one. In any case, one should assume a particular expression for the potential energy of the system which quantifies the particle interactions. Many types of potential energy functions have been proposed depending on the system studied and include two-body or pair potentials, such as the well-known Lennard-Jones potential and multi-body potentials like the Tersoff one [60]. Molecular simulations have been used by Dereli et al. [16], Jeng et al. [43], Sammalkorpi et al. [91], WenXing et al. [114] and Yao and Lordi [121] to model the mechanical behavior of CNT under prescribed loads.

Overall, it is important to note that the significant variations in the values for the mechanical properties of CNT, shown in this chapter, reflect the difficulties encountered in experimental, analytical and computational methods used to measure and/or compute them.
Consequently, this dissertation views the uncertainty in the CNT properties as a critical factor that needs to be quantified to evaluate its effect on the mechanical properties of nanocomposites, which is the subject of this dissertation. In this context, it should be mentioned that the influence of the medium in which CNT are dispersed on their properties is significant. Therefore, Chapter 3 of this dissertation discusses the reinforcement function of CNT in nanocomposites by realistically describing the parameters that influence their incorporation in other materials. In this manner, CNT are treated as part of a larger material system with which they interact and which affects their mechanical reinforcement capability.
Chapter 3

Polymer Nanocomposites (PNC)

This chapter presents the structure, fabrication procedures, experimental characterization, and modeling of the mechanical behavior of polymer nanocomposites (PNC). To facilitate the understanding of this new kind of nanomaterial, the chapter analyzes the role of polymers in modern engineering applications. Next, Chapter 3 describes the experimental procedures followed to mix carbon nanotubes (CNT) with polymers. In addition, this chapter investigates the structure of PNC at the nano-/micro-scales and identifies uncertainties related to the dispersion of the inclusion phase. Finally, Chapter 3 presents the experimental techniques and modeling methods that are used to determine the mechanical properties of PNC.
3.1 Polymers as engineering materials

Polymers, such as plastics, are common engineering materials used in a variety of applications because of their chemical, physical, and mechanical properties. The name “polymers” is a combination of the Greek words poly that means “many” and meros which, in this context means “units.” Therefore, polymers are materials that consist of many, actually thousands, of repeating units.

3.1.1 Chemical structure

From a chemical point of view, polymers are molecular systems that consist of a number of monomers connected by covalent bonds. A monomer is a small molecule composed of one chemical unit. For example, ethylene is a monomer and a group of such monomers forms polyethylene, as shown symbolically in Figure 3.1.

![Polyethylene structure diagram](image)

Figure 3.1: Polyethylene as an example of a polymer composed of $n$ ethylene monomers.

Among monomers the chemical reaction which leads to the formation of polymers is called polymerization [52]. To describe polymerization, polyethylene is used as an example. During polymerization the double bond between the two carbon atoms in the ethylene
monomer is converted, under appropriate conditions, to a single covalent bond. Therefore, each of the two carbon atoms has one available electron to form a new covalent bond with a neighboring carbon atom from another monomer. The result is a molecular chain of \( n \) monomers which constitutes the polymer.

Furthermore, polyethylene is an example of a "homopolymer" because all of its repeating units are identical. However, polymerization between chemical units that consist of more than one monomer is also possible, resulting in "copolymers". In particular, the copolymerization process can produce "random copolymers," in which there is no discernible pattern in the sequence of the participating monomers, as well as "alternating" and "block" copolymers, in which there is an alternative sequence and groups of distinct repeating units, respectively.

Regarding the shape of polymer molecules, the three major types are shown in Figure 3.2. "Linear" polymers are long curved chains of repeating chemical units having various lengths. "Branched" polymers consist of a backbone chain on which shorter side chains are attached. Finally, "cross-linked" polymers consist of a network of bonded and entangled molecular chains.

Based on their thermal properties, polymers can be divided into two groups [76]. Specifically, polymers are called "thermoplastics" if they melt when sufficiently heated, while "thermosets" cannot be melted. The linear and branched polymers, shown in Figure 3.2, are examples of thermoplastics, while the cross-linked ones are thermosets. In thermoplastics individual molecular chains can be separated from the rest of the bulk material above
Figure 3.2: The three types of polymers based on the shape of their molecular chains: linear, branched and cross-linked.

a certain temperature. This type of separation is not feasible in thermosets because of the entanglement of the molecular chains in their structure.

3.1.2 Physical, thermal and mechanical properties

The solubility, flexibility, stiffness and strength of polymers depend on their physical, thermal and mechanical properties. Therefore, the quantification of these properties is important for engineering applications.

In practice, the molecular weight (MW) of a polymer needs to be determined. Monomers have low molecular weight, but during the polymerization process the MW of the resulting monomer chains increases. However, it is difficult to measure the exact MW of a specific polymer because the participating chemical units at the branching and end points behave
in a different way compared to the ones in the main molecular chains. A parameter used to evaluate the polymerization process is called "degree of polymerization;" it can be expressed as the average MW of the polymer divided by the MW of the chemical units in the chains [107]. Nevertheless, MW distributions in lieu of exact values are usually suggested in actual fabrication procedures reported in the literature.

Furthermore, the molecular structure of polymers affects their mechanical properties. In particular, it has been reported that the entanglement and branching of molecular chains enhance the stiffness and strength of polymers [107]. This type of reinforcement occurs because it is in general harder to separate the molecular chains, in the case that multiple cross-links exist. In addition, crystals in the polymer structure result in improvement of their mechanical properties. Atomic crystals exist only in thermoplastics, along with amorphous regions that consist of randomly oriented and entangled molecular chains.

The mechanical properties of polymers depend also on temperature. In particular, each polymer is characterized by a specific temperature called "glass transition temperature", $T_g$. In fact, the polymer's stiffness and strength below $T_g$ decrease slowly with increasing temperature and the overall material behavior is brittle. However, for temperatures higher than $T_g$, polymers become ductile and a significant decrease of their stiffness and strength is observed. It has been reported that the more amorphous the polymer structure is, the more significant is the decrease in its mechanical properties for temperatures higher than $T_g$ [76]. Table 3.1 presents representative values for the most important mechanical properties and the glass transition temperatures of some polymers used in engineering applications.
Table 3.1: Representative values for the mechanical properties and glass transition temperatures of some polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Density (g/cm³)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>70</td>
<td>2.6</td>
<td>1.2</td>
<td>175</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>40</td>
<td>1.9</td>
<td>0.9</td>
<td>-10</td>
</tr>
<tr>
<td>Polyester</td>
<td>9</td>
<td>0.7</td>
<td>1.2</td>
<td>150</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>10</td>
<td>0.2</td>
<td>0.9</td>
<td>-30</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>45</td>
<td>3</td>
<td>1.05</td>
<td>100</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>73</td>
<td>2.1</td>
<td>1.1</td>
<td>50</td>
</tr>
<tr>
<td>PVC</td>
<td>45</td>
<td>2.5</td>
<td>1.3</td>
<td>85</td>
</tr>
</tbody>
</table>

3.2 Polymer nanocomposites

Based on the information presented in Table 3.1, it can be concluded that polymers are lightweight materials with moderate mechanical properties compared to others, such as the ones presented in Table 2.1. Nevertheless, polymers have been widely used in a variety of applications because of their relatively simple and cost-effective fabrication procedures, molecular structures and physical properties.

A particularly interesting application of polymers is their incorporation in larger molecular systems, and the formation of novel composite material structures with unique combinations of properties. Polymer nanocomposites (PNC) are an example of such material systems that consist of polymers mixed with other phases, one or more of which have at least one characteristic dimension on the order of 1-100 nm. Polymers used in PNC include epoxy resins, polypropylene (PP), polyvinyl alcohol (PVA), polyethylene (PE), polystyrene
(PS) and others. PNC also include nanoinclusions, such as individual SWCNT, SWCNT ropes and bundles, MWCNT, fullerenes and nanoparticles. The role of the inclusion phases in PNC is to enhance the mechanical, electrical, physical and chemical properties of the polymer matrix. In this dissertation, the mechanical behavior of PNC that comprise polymer matrices reinforced with SWCNT is modeled. Therefore, any subsequent use of the term “PNC” refers to this kind of material.

Although the mechanical properties of PNC are better compared to the ones of the neat polymers, they are often worse than pertinent values reported in the literature for polymers reinforced with microscale-type fibers, such as the ones presented in Table 2.2 [72]. Three major issues that are responsible for this relatively poor mechanical behavior have been identified in the literature and are analyzed next. The first involves the dispersion of the SWCNT in polymers. The second includes the load transfer mechanisms between the polymer and the nanotubes and the third deals with the size, shape and orientation of the inclusion phase.

### 3.2.1 Dispersion of carbon nanotubes

To enhance the mechanical properties of PNC, it is important to disperse CNT uniformly in the matrix. This uniform or homogeneous dispersion, as it is frequently called in the literature, would eliminate any weak regions in the composite’s structure. At a local level, the existence of weaker regions is potentially hazardous to the bulk behavior of the composite, since stresses can exceed the material’s strength at these locations and lead to the initiation
of failure mechanisms, such as cracks.

Pristine SWCNT are in general insoluble in polymers because of their atomically smooth surface [86]. The sidewalls of SWCNT are essentially one carbon atom thick and, therefore, intrinsic Van der Waals forces cause electrostatic interactions among adjacent nanotubes. These interactions are in general weak and lead to the formation of SWCNT bundles while they also prevent their uniform dispersion in the polymer matrix. To overcome this difficulty, a number of procedures have been proposed in the literature to improve the dispersion of SWCNT in polymers and are presented next.

*Sonication* methods are frequently used to achieve better dispersion of CNT in polymers. During sonication, sound waves disrupt and disperse biological materials. For example, Biercuk et al. [8] use a 48 hour long sonication method to disperse CNT in a composite material. However, it has also been reported that lengthy sonication is responsible for CNT damages and cuts, which must be avoided to harness the full potential offered by this kind of nanomaterial [86]. Therefore, the duration of sonication methods is usually on the order of minutes and, in this way, it is commonly used as part of multistage PNC fabrication methods [11, 14, 79, 86, 127].

*In situ polymerization* has also been proposed to disperse CNT in polymers. Park et al. [81] report that the addition of chemical agents in the CNT-polymer mixture during sonication assists the polymerization of the monomers in the solution. In addition, this process does not require any prior chemical modification of the CNT sidewalls. In situ polymerization procedures have been also reported by Barraza et al. [5] and Kumar et al.
Surfactants are frequently used to assist the dispersion of CNT in polymers. Surfactants are chemical wetting agents that lower the interfacial tension between two liquids, allowing better dispersion. The term “surfactants” is used to denote surface active agents that usually consist of hydrophilic “heads” and hydrophobic “tails.” Gong et al. [32] use a type of surfactant to disperse CNT in an epoxy matrix and they claim good dispersion of CNT, as a result of the repulsive forces between them created by the surfactant agent. According to the same authors, this type of repulsion seems to be stronger than the intrinsic van der Waals forces that typically hold the CNT into bundles.

Finally, chemical treatment of the surface of the SWCNT has been proposed to improve their dispersion in polymers. Section 2.4.2 presents the role of functionalization in the solubility and adhesion of SWCNT in PNC. This method has been implemented in the PNC fabrication procedures presented by Zhu et al. [127] and Paiva et al. [79]. The PNC examined in these two articles are further used to calibrate the various parameters of the method developed in this dissertation, since critical details about their fabrication procedure are known.

In current PNC fabrication procedures a combination of two or more of the previously described dispersion methods is used to achieve good solubility of SWCNT in polymer matrices. In addition, mixing process, such as the high shear mixing one, are often used to assist the breaking of large agglomerates of SWCNT.

A group of articles found in the literature claim uniform/homogeneous dispersion of
SWCNT in polymers based on the use of dispersion methods similar to the ones described in this section. For example, the articles by Ramasubramaniam et al. [86], Paiva et al. [79], and Chen et al. [11] report homogeneous dispersions. This conclusion is usually based on images taken by conventional microscopy techniques ranging from optical microscopes (OM) to scanning electron microscopes (SEM), scanning probe microscopes (SPM) and atomic force microscopes (AFM). However, Loos et al. [62] suggest that this kind of imaging shows only the surface or a cross-section of a larger three-dimensional structure and thus, it is difficult to extract reliable information about the dispersion of CNT in the entire volume. The same authors also report that there is a direct correlation between the type of microscopy used and the number of nanotubes observed. For examples, Loos et al. mention that the SEM images, which are frequently used to evaluate the dispersion properties of SWCNT in polymers, provide information that depends on the specific settings of the microscope. Therefore, it should be noted at this point that there are reported uncertainties pertinent to the dispersion of SWCNT in polymers, which are modeled by the method developed in this dissertation.

Moreover, Zhu et al. [127] report that as the volume fraction of SWCNT in polymers increases, higher viscosity and void defects appear in the PNC structure. Hence, it can be concluded that the assumption of uniform/homogeneous dispersion needs to be supported by appropriate imaging analysis and experimental evidence. In addition, the effect of the non-uniform dispersion of nanofillers on the mechanical properties of PNC needs to be investigated to provide a realistic description of the material's structure at the nano-
/microscale. The method presented in this dissertation models the uncertainty in the spatial distribution and dispersion of the SWCNT in polymers.

### 3.2.2 Load transfer

An important parameter that affects the mechanical behavior of PNC is the load transfer between the polymer matrix and the reinforcing SWCNT. To take advantage of the mechanical properties of SWCNT, the applied mechanical loads on the PNC must be efficiently transferred from the polymer to the reinforcement phase. This load transfer strongly depends on the interfacial characteristics between the different phases in PNC. In practice, strong covalent bonds and/or non-covalent electrostatic interactions determine the strength of the interface. In the case of covalent bonding, section 2.4.2 of this dissertation explains that the functionalization of SWCNT chemically modifies their surfaces and affects their mechanical properties and reinforcement capabilities. Moreover, the electrostatic interactions between the phases of PNC are in general weak and, therefore, poor interfacial bonding is achieved.

To assess the quality of the interfacial interaction in PNC and to quantify the adhesion strength, a number of experimental techniques have been proposed. However, it should be noted that the direct measurement of the SWCNT-polymer interfacial strength is difficult to achieve due to difficulties that exist in handling individual SWCNT.

Cooper et al. [14] present a technique to quantify the adhesion strength between SWCNT and polymers using a scanning probe microscope tip and transmission electron
microscopy images. The authors report that SWCNT tend to bundle in ropes, and the strength of the SWCNT rope-polymer interface is determined by appropriate pull-out tests. The authors argue that the measured interface strength is higher compared to fiber reinforced polymers, and they explain that this is caused by the covalent bonds between the polymer and the SWCNT. However, Ajayan et al. [1] describe tension and compression tests of PNC consisting of epoxy matrix and SWCNT, and they report weak coupling between the two phases. Specifically, the authors analyze fracture surfaces and claim that pull-out of SWCNT ropes instead of individual SWCNT is observed. The poor interfacial properties are subsequently determined by using energy computations. Furthermore, indirect assessment of the SWCNT-polymer interfacial strength can be achieved by measuring the mechanical properties of PNC using dynamical mechanical analysis (DMA) [34] (see section 3.2.4.2 of this chapter).

Analytical models have been also developed to compute values for the CNT-polymer interface strength. Wagner [111] expands the Kelly-Tyson model to determine the interfacial strength of SWCNT-reinforced polymers. The same author provides an analytical expression that yields values for the strength of the interface based on the tensile properties of the SWCNT and their geometrical characteristics.

Moreover, continuum cohesive zone models (CZM) have been used to study the interface properties in PNC. Jiang et al. [44] use CZM to investigate the CNT-polymer interfaces created only by Van der Waals forces. These forces are modeled in this article by using arbitrary pair potential functions for CNT in infinite and finite matrices. The authors provide
an analytical solution for the tensile cohesive stresses that is subsequently used to compute values of the interfacial strength. Namilae and Chandra [70] also use CZM in a hierarchical multiscale scheme. Specifically, the authors use MD simulations of pull-out tests to obtain values for some parameters that appear in the analytical CZM, which are subsequently incorporated in a finite element model that determines the macroscopic mechanical behavior of the PNC. The proposed results show that the composite’s Young’s modulus decreases significantly as the value for the interfacial strength is reduced.

To overcome the difficulties appearing in experimental techniques and to avoid the critical assumptions made in continuum models, computational methods have been developed. Frankland et al. [25] use molecular simulations to investigate the effect of chemical cross-links between SWCNT and polymers on the interfacial strength, as shown in Figure 3.3. The authors suggest that an improvement in the adhesion between the two phases is achieved as the density of the cross-links increases. Gou et al. [33] also use molecular simulations to study the load transfer mechanisms between SWCNT-ropes and polymers, as well as between the individual tubes in the ropes. The pull-out simulations performed in this article suggest that SWCNT have stronger interactions with each other in the ropes than with the polymer matrix. The authors report values for the interfacial stresses computed by an analytical expression that takes into account the geometric properties of the nanotubes as well as the pull-out energies.

Overall, it can be concluded that the interfacial characteristics between the polymer and the reinforcing phases in PNC must be taken into consideration when computing values
Figure 3.3: Chemical cross-links in the interfacial zone between a single-wall carbon nanotube and a polymer that can increase the interfacial strength in PNC as reported in [25].

for the mechanical properties of PNC. The characterization/modeling method presented in this dissertation provides a strategy to incorporate this information on the determined mechanical behavior of PNC.

3.2.3 Shape, orientation distribution and size of the inclusion phases

The shape of the reinforcement phases affects the macroscopic material behavior of PNC. Due to their high aspect ratio and large surface energies, SWCNT in polymers exist as entangled ropes and bundles. Zhu et al. [127], report that an investigation of the fracture surfaces of PNC that have been axially loaded reveals SWCNT bundles with sizes larger than 50 nm. The authors argue that intermolecular hydrogen bonds and possible cross-links are responsible for this type of SWCNT clustering. Furthermore, Zhu et al. mention that SWCNT ropes are usually curved, but they can be partially stretched as the matrix is axially loaded. In addition, Li et al. [57] claim that curved SWCNT bundles and agglom-
erates of bundles constitute the actual reinforcement phase in PNC rather than individual straight SWCNT. The same authors, therefore, propose that the mechanical properties of this type of "nanoagglomerates" should be used when modeling the mechanical behavior of PNC. Li et al. also suggest that as the SWCNT volume fraction increases, the number of nanoagglomerates in the polymer becomes larger.

Based on the information presented in this section, it can be concluded that the PNC structure is characterized by the existence of a number of heterogeneities. Figure 3.4 shows two images of actual PNC structures reported in the literature. It can be seen in Figure 3.4 that agglomerates of various sizes (above) and networks of entangled SWCNT bundles (below) are observed in practice. Therefore, it is important to investigate the effect of the spatial distribution of SWCNT in polymers on the mechanical properties of PNC to realistically predict their behavior in actual applications, as shown in this dissertation.

The orientation distribution of SWCNT in polymer matrices is an additional parameter that affects the mechanical properties of PNC. Because of their large aspect ratios and nanoscale dimensions, CNT are often curved and entangled. Therefore, it is difficult to align them in specific directions as usually made in microcomposites, in which fibers are placed in specific directions. Orientation distributions computed based on Raman spectra have been suggested by Bhattacharyya et al. [7]. These authors show that nanotube orientation distributions strongly depend on the specific types of CNT and polymers, as well as on the fabrication procedure used. The effect of the orientation of SWCNT in polymers has been taken into account in the method developed in this dissertation.
Finally, the size of the inclusions in a composite is an additional factor that affects the overall mechanical properties. In the case of SWCNT-reinforced polymers, the nanoscale dimensions of the inclusions require a size-analysis that is more difficult compared to traditional microcomposites. In addition, the size of the actual nano-inclusions strongly depends on the length scale of observation and on the particular imaging method used [62]. The size of the inclusions in PNC is usually taken into consideration in modeling by using informa-
tion about the aspect ratios and the weight percentage or volume fraction of the SWCNT. The method developed in this dissertation uses values for the SWCNT aspect ratios and volume fractions based on pertinent experimental information.

3.2.4 Characterization of mechanical properties

The successful incorporation of PNC in larger material systems and structures relies on the characterization of their properties. For mechanical engineering purposes, the properties that need to be quantified include mainly the tensile modulus and strength and their dependence on the SWCNT volume fraction, dispersion, agglomeration, aspect ratios and orientation. Additionally, the load transfer between the polymer matrices and the SWCNT is an important parameter that must be evaluated. This section presents the most widely used experimental techniques to characterize the mechanical properties of PNC.

3.2.4.1 Tensile testing

Tensile testing is performed on almost all types of PNC that are produced for mechanical engineering applications. Estimates for the material’s Young’s modulus, yield and ultimate strength are obtained from stress-strain curves similar to the one presented in Figure 3.5.

Tensile tests for PNC have been reported in the literature. Zhang et al. [126] conducted tensile tests at room temperature on samples of polyvinyl alcohol (PVA) reinforced with 5 weight percent (5 wt%) SWCNT produced by the HiPCO method. Five samples of the PNC were tested and the mean measured value for the tensile yield strength of the PNC
Figure 3.5: An example of a stress-strain curve obtained by a tensile test experiment. Stress values are given in the vertical and strain values in the horizontal axis. The values $\sigma_{\text{max}}$ and $\sigma_{\text{yield}}$ correspond to the ultimate and yield stresses respectively, while $E$ is the Young’s modulus.

was found to be 78% higher compared to the value for the neat PVA. Moreover, the mean value for the Young’s modulus of the PNC increased 110% compared to the PVA matrix. Based on these findings, the authors claim that the load transfer between the polymer and the SWCNT was good, and to verify this assumption they provide further experimental evidence in the form of Raman spectra. In addition, optical microscopy images of the tested PNC reported in the same article do not show SWCNT agglomerates. However, this observation is not supported at lower length scales, since the authors refer to pertinent results by SEM microscopy, which reveal SWCNT bundles and agglomerates.

Moreover, Gojny et al. [31] also conducted tensile tests on PNC consisting of a mod-
ified DGEBA-based epoxy resin L135i and SWCNT that were produced by the chemical vapor deposition method. Three values for the weight percentage of SWCNT in the polymer equal to 0.05%, 0.1% and 0.3% were used. The authors report that the Young’s modulus of the neat epoxy increases in approximately linear way as the number of SWCNT increases. Eight samples for each SWCNT concentration were tested and the maximum reported mean value for the Young’s modulus of the PNC was measured 8% higher compared to the value of the neat polymer. The corresponding increase in the ultimate tensile strength was found equal to 5.4%. These experimental results were obtained for very low values of the SWCNT concentration, and consequently, it is difficult to accurately assess their reinforcement role. Nevertheless, Gojny et al. mention that even for these small numbers of dispersed SWCNT, TEM images reveal the existence of agglomerates having varying diameters and shapes. Consequently, the premise of non-uniform dispersion of SWCNT made in this dissertation is supported by experimental evidence and is modeled by the proposed method presented in the following chapters.

Furthermore, Paiva et al. [79] and Zhu et al. [127] report values for the Young’s modulus and tensile strength of PNC measured by tensile tests. Both articles use two values for the number of SWCNT in the polymer, and, thus, they enable the investigation of the effect of the concentration of SWCNT on the mechanical properties of PNC. The experimental findings of these two articles serve as a basis for comparison with the proposed results included in this dissertation. Therefore, Chapter 5 provides a detailed description of the fabrication and testing procedures for the PNC studied in these two articles to support
the assumptions made in the method developed in this dissertation.

3.2.4.2 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is an experimental technique commonly used to characterize the material properties of polymers [66]. In DMA, an oscillating force is applied on a sample of the material under investigation. Figure 3.6 shows an example of the applied stress and the measured material response in DMA. In Figure 3.6, it can be seen that there is a phase lag $\delta$ between the applied and response stress curves. This lag indicates loss of energy as heat (damping). In addition, DMA provides a measure of the modulus of the tested material as a function of temperature. Specifically, the determined modulus in DMA is not equal to the Young’s modulus described in section 3.2.4.1. The DMA modulus is a complex modulus $E^*$, composed of an elastic modulus $E'$ and a loss modulus $E''$, as shown in the schematic representation of Figure 3.6. These two moduli characterize the material’s response to the applied load, since the elastic modulus quantifies the ability to store energy and the loss modulus represents the losses in energy due to heat dissipation. The ratio of the two moduli measured in a DMA test (i.e. the tangent of the angle $\delta$ shown in Figure 3.6) is called damping.

Fidelus et al. [21] report DMA tests on PNC consisting of epoxy LY564 and Epon 815 reinforced with SWCNT produced by the HiPCO method. Two SWCNT contents for both material systems were examined and were equal to 0.01 and 0.05 wt%. The DMA results show the variation of the storage modulus and damping for both PNC and for a range
of temperatures between 50 and 130 °C. In fact, it is reported that the storage modulus increases and the damping decreases as the SWCNT content increases for both PNC. For example, Figure 3.7 shows some of the DMA results reported in this article. Based on the DMA results, Fidelus et al. suggest that the incorporation of SWCNT in polymers resulted in enhanced mechanical behavior of the PNC. However, only a moderate 8% increase in the value of the storage modulus of the PNC with respect to the neat polymers is measured. Fidelus et al. mention that a possible explanation for this relatively low increase in the storage modulus could be attributed to the presence of agglomerates of SWCNT ropes, observed in optical and SEM images.

Moreover, Miyagawa et al. [69] also conducted DMA to determine the storage modulus of PNC composed of epoxy and epoxidized linseed oil, reinforced with functionalized SWCNT produced using the HiPCO method. The temperatures used in these DMA tests
Figure 3.7: Sample results for the storage modulus and damping of a PNC material reported by Fidelus et al. [21]. As it can be seen, the incorporation of SWCNT in the polymer results in a moderate increase of the storage modulus and a decrease of the damping.

were in the range of 0-170 °C. The storage modulus of the PNC was measured 25% higher compared to the value of the neat polymer. Based on this result, the authors suggest that the functionalized SWCNT were homogeneously dispersed.

Nevertheless, an analysis of the reported DMA characterization results in the two articles mentioned in this section shows that the incorporation of small amounts of SWCNT in polymers causes a moderate enhancement of the mechanical properties of PNC. One of the parameters responsible for the insufficient reinforcement of PNC is the non-uniform dispersion of the nanofillers in the polymer matrix. This type of nanotube dispersion creates local weak regions that decrease the overall structural integrity of the PNC. Consequently, it is important to model the effect of the SWCNT agglomeration on the mechanical behavior of PNC. To this aim, the method developed in this dissertation provides a model that quantifies the non-uniform dispersion and spatial distribution of SWCNT in polymers and
yields estimates for the mechanical properties of PNC.

### 3.2.4.3 Nanoindentation

Nanoindentation tests have been proposed in the literature to characterize the Young’s modulus of PNC. In this kind of indentation at the nanoscale, an indenter, which typically has spherical or pyramidal shape, touches the material of interest. Figure 3.8 shows typical indenters used in nanoindentation tests. The resistance of the material to the indenter is measured as a function of the penetration depth. Figure 3.9 presents the loading-unloading path followed during nanoindentation. The Young’s modulus of the tested material is measured using load curves similar to the one shown in Figure 3.9 and by taking into account the mechanical properties of the indenter. Nevertheless, there are many models to compute values for the Young’s modulus using nanoindentation findings, because of uncertainties in parameters, such as the exact contact area and the analytical form of the loading curve [22].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Berkovich</th>
<th>Cube-corner</th>
<th>Cone</th>
<th>Spherical</th>
<th>Vickers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shape</strong></td>
<td><img src="image" alt="Berkovich" /></td>
<td><img src="image" alt="Cube-corner" /></td>
<td><img src="image" alt="Cone" /></td>
<td><img src="image" alt="Spherical" /></td>
<td><img src="image" alt="Vickers" /></td>
</tr>
<tr>
<td>C-f angle</td>
<td>65.35°</td>
<td>35.264°</td>
<td>—</td>
<td>—</td>
<td>68°</td>
</tr>
<tr>
<td>Projected</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact area</td>
<td>24.5600d²</td>
<td>2.5981d²</td>
<td>πa²</td>
<td>πa²</td>
<td>24.5044d²</td>
</tr>
</tbody>
</table>

Figure 3.8: Typical shapes for the indenters used in nanoindentation tests. C-f angle is the face angle of the indenter, d is the indentation depth and a is the tip radius in conical and spherical indenters [83].
Dutta et al. [18] performed nanoindentation tests on PNC consisting of an epoxy resin EPON 862 and SWCNT produced using the laser ablation method. Three SWCNT contents equal to 0.1, 0.5 and 1 wt% were used. Ten samples of PNC for each value of the SWCNT concentration were tested. The analysis of the nanoindentation results shows that as the SWCNT content increases, the Young’s modulus of the PNC moderately increases. However, the authors also report that the computed values for the Young’s modulus of the
PNC samples decrease as the penetration depth increases for all three SWCNT concentrations in the polymer. Dutta et al. suggest that this trend is observed due to the aggregation of SWCNT near the surface. Furthermore, the nanoindentation results reported in this article have not been found consistent with pertinent tensile test findings reported by the same authors. Difficulties related to the testing procedures are considered by Dutta et al. responsible for this discrepancy.

Moreover, Li et al. [57] determine the Young’s modulus of PNC comprising an ester resin and functionalized SWCNT produced by the arc discharge method using nanoindentation. Three SWCNT concentrations equal to 1, 3 and 5 wt% were used. A diamond Berkovich (see Figure 3.8) indenter tip was used to penetrate the surface of the PNC samples. In total, ten indentations for each sample were performed. Figure 3.10, shows an example of the indenter’s impression on the tested samples at the peak load. The authors report that as the amount of SWCNT in polymers increases, the indentation depth decreases and the computed value for the Young’s modulus of the tested sample increases. In addition, the authors found that the determined Young’s modulus values remain constant with increasing penetration depth of the nanoindenter. Therefore, Li et al. claim that the SWCNT were well dispersed in the tested PNC samples. However, SEM images reported in this article clearly show the existence of nanotube bundles and agglomerates for the samples with concentrations 3 and 5 wt%. In addition, the authors observe that there is no significant increase in the computed values of the Young’s modulus as the concentration of SWCNT becomes greater than 3 wt%. Therefore, they suggest that there is an
upper limit on the amount of SWCNT that should be mixed with polymers in PNC to avoid agglomeration due to the interactions between the nanotubes.

Figure 3.10: Atomic force microscope images of the nanoindenter’s impression on the PNC samples at the maximum applied load [57].

In summary, it should be noted that the use of multiple nanoindentations on the same sample of PNC provides values for the Young’s modulus at a local level. The spatial variation of the Young’s modulus in the sample reflects differences in the local concentration of SWCNT in polymers. Consequently, nanoindentation findings can be used to investigate the effect of the local variation of the Young’s modulus on the overall mechanical behavior of PNC. To this aim, the method developed in this dissertation has been adapted to use nanoindentation-type results to characterize the mechanical properties of PNC.
3.2.5 Modeling of mechanical properties

Modeling the mechanical properties of PNC is a challenging task due to the length scales involved. The PNC modeled in this dissertation comprise polymers reinforced with nanoscale fillers that have the form of individual straight or curved CNT, bundles or ropes of CNT and agglomerates of bundles, as presented in section 3.2.3 of this chapter. In addition, the sidewall properties of CNT create new kinds of interfaces with the polymer matrix in PNC. Therefore, information that spans the range from atomistic to macroscale dimensions is needed to model accurately and reliably the effect of "nanofillers" on the mechanical properties of PNC.

To deal with the difficulties in modeling the mechanical properties of PNC, a new type of engineering mechanics called "nanomechanics" has been developed. In nanomechanics, "multiscale" methods (MM), which are based on the use of various models to determine the mechanical behavior of nanomaterials, are used. Models that compute values for parameters in different length scales are used in MM to overcome the difficulties encountered in continuum methods to accurately describe phenomena that occur in the atomic level, and the limitations of modern simulation methods to analyze large material regions. Hence, the goal of MM is to bridge the length scales involved in the investigation of the behavior and properties of nanomaterials. To achieve this goal, a coarse-to-fine decomposition is usually performed. This decomposition separates the domain of interest in regions in which different methods are used. For example, a common practice in modeling of nanomaterials is to combine molecular simulations with continuum methods to describe the evolution of a
phenomenon, such as fracture.

According to the way that information is exchanged among the different modeling components in nanomechanics applications, there are two groups of MM [60]. In hierarchical MM, information obtained in the small scale using, for example, molecular dynamics (MD) simulations, is subsequently passed to other models that perform computations at higher length scales. The proposed method in this dissertation, a hierarchical MM, is described in Chapter 4. In concurrent methods, the determination of material properties is based on the simultaneous use of, quantum, molecular and continuum models, for example. These methods are more difficult to implement, since there is no a priori dependence of a particular model on others. Instead, some “handshaking” regions, as they are often called, are defined in concurrent methods to link the various models used. Examples of concurrent MM can be found in the book by Liu et al. [59]. Furthermore, the methods presented in this section focus on modeling of the mechanical behavior of PNC and provide information about nanomechanics applications.

In the case of PNC, various models have been suggested in the literature to determine their mechanical properties. Frankland et al. [26] present stress-strain curves for PNC similar to the one shown in Figure 3.5, using MD simulations. The authors clarify, though, that the derived results do not intend to simulate the yielding of carbon nanotubes. The polymer in the simulations is amorphous polyethylene (PE) (see Figure 3.1), and the reinforcement phase consists of (10, 10) SWCNT that are capped with halves of $C_{240}$ molecules. Two different configurations, defined by assuming that the PNC have periodic material struc-
ture, are examined in this article and consist of infinitely long and short carbon nanotubes respectively. The interfacial interactions between the polymer matrix and the reinforcing straight SWCNT are modeled using a specific analytical function. Moreover, Frankland et al. use two loading conditions corresponding to pure longitudinal and transverse deformations. Stresses in the PNC model described in this article are computed by equating the internal energy of the system computed by MD and the strain energy of the solid, which is known by means of the elasticity theory. The stress and strain values computed by the simulation methods are subsequently compared to values obtained by using the rule of mixtures technique. The results shown in this article suggest that the reinforcement role of SWCNT in polymers is more important in the case of longitudinal loading (particularly for long nanotubes) than in transverse loading. Furthermore, the MD simulation results are in all cases lower compared to the rule of mixtures ones. This fact shows that the direct use of analytical models to determine the properties of PNC leads to errors because critical information about the physics of the problem is not taken into consideration.

The method proposed by Frankland et al., is based on the assumption of aligned and straight SWCNT in a periodic medium. Nevertheless, it has been shown in this chapter that the orientation distribution and shape of the inclusions determined by images of actual PNC deviates from this idealized picture. Therefore, a more realistic approach is needed to capture the effect of carbon nanotubes on the mechanical properties of PNC.

Odegard et al. [73] present a MM that includes MD simulations, an equivalent truss model and a continuum micromechanics method to determine the dependence of the me-
chanical properties of PNC on the SWCNT volume fraction, aspect ratio and orientation distribution. Figure 3.11 presents the modeling components of the MM proposed in their article. It should be noted here that the method proposed in this dissertation uses the information obtained by the MM developed by Odegard et al. to determine the overall mechanical properties of PNC. Therefore, a qualitative description of Odegard's model is given here, while the quantitative part is presented and used in subsequent chapters.

Figure 3.11: The three-stage multiscale method proposed by Odegard et al. [73]. The molecular model consisting of SWCNT mixed with a polymer is linked to an equivalent continuum model that comprises a solid fiber with properties that represent the SWCNT and the interphase interactions. To achieve this representation an equivalent-truss model is used as a link between the molecular and continuum model.

In the three-stage MM developed by Odegard et al. and shown in Figure 3.11, MD simulations are used to generate the equilibrium structure of two PNC material systems
consisting of a thermoplastic polyimide in the first, and a colorless polyimide in the second case, reinforced with (6, 6) SWCNT. Furthermore, a solid, cylindrical, linear elastic, homogeneous fiber is defined in the continuum model, and its elastic parameters are defined by equating the energies of the molecular and continuum models. To this end, an equivalent truss model serves as the intermediate link between the molecular and continuum models. Next, by applying a set of boundary conditions to both the truss and continuum models, the elastic parameters of the solid effective fibers are determined. The mechanical properties of these fibers are subsequently used in the Mori-Tanaka micromechanics method (see Chapter 4) to determine the mechanical behavior of PNC. Specifically, the effect of carbon nanotube orientation, length and volume fraction on the mechanical properties of PNC is investigated. Both aligned and random SWCNT distributions are used in the computations. Moreover, experimental DMA (see section 3.2.4.2) is applied on samples of the second PNC material system, and the storage modulus measured at room temperature is assumed to be equal to the Young’s modulus. Based on this assumption, the authors report differences between the experimental and modeling results. The authors suggest that the reason for this discrepancy is the existence of bundles and agglomerates of SWCNT in the polymer. Nevertheless, the MM presented by Odegard et al. succeeds in passing the molecular information into the continuum model and this is why it is used in the method developed in this dissertation.

Furthermore, finite element (FE) methods have been used to compute the mechanical properties of PNC. A multiscale FE method for determining the mechanical properties of
PNC is proposed in this dissertation and is described in following chapters. An example of a FE model has been reported by Song and Youn [99] who use an asymptotic expansion homogenization method in a control volume finite element method (CVFEM) to determine the mechanical properties of polymers reinforced with CNT. In the homogenization method developed by Song and Youn, the CNT are assumed to be homogeneously dispersed, perfectly bonded and aligned, while no intertube interactions are taken into account. In addition, the nanocomposite is assumed to be periodic and, thus, the volume analyzed is shown in Figure 3.12.

![Diagram of nanocomposite](image)

Figure 3.12: The material volume element used in the finite elements model developed by Song and Youn [99]. A long and straight carbon nanotube inside a polymer box is representative of the assumed periodic structure of the polymer nanocomposite.

The homogenization method developed by Song and Youn results in a continuum formulation which is subsequently incorporated in a FE method that yields the mechanical
properties of PNC. The numerically derived results are then compared to values for the mechanical properties computed by using the Halpin-Tsai micromechanics theory and measured by pertinent experiments. As reported by the authors, the FE method results agree with the values computed by the particular micromechanics method but differ from the experimental ones. To explain this discrepancy, Song and Youn suggest that the assumption of straight CNT is not accurate since image analysis shows that they are usually curved. In addition, the authors believe that there is uncertainty in the values of the material properties of CNT which affects the proposed results in their article. However, as it is explained in Chapter 4 of the dissertation, the assumption of a periodic structure is not accurate in the case of PNC due to the dispersion properties of CNT in polymers.

Another example of a FE model has been given by Liu and Chen [61] who propose a three-dimensional elasticity model to study the mechanical behavior of PNC. In their article, three material volume elements, similar to the one presented in Figure 3.12, are defined. Both the CNT and the matrix in these volume elements are assumed to be linearly elastic, isotropic, homogeneous and perfectly bonded to each other. Three loading cases that correspond to axial/lateral stretch and torsion are applied in the defined material volume elements to determine expressions for their elastic constant using elasticity solutions. Then the mechanical properties of the PNC are determined using both the rule of mixtures and a FEM for long and short CNT. In the case of long CNT, the two approaches yield identical results which show enhanced mechanical properties for the polymer reinforced with nanotubes. However, there are differences between the rule of mixtures and the FEM
solution in the case of short fibers. These differences imply that the direct application of continuum methods in modeling of PNC is not always successful, because of important information at the lower length scales that is ignored.

In addition, Ashrafi and Hubert [3] use a FE method to determine the mechanical properties of PNC in which the reinforcement phase consists of twisted SWCNT nano-arrays. The authors in this article suggest that to harness fully the potential of SWCNT in enhancing the mechanical behavior of modern composite materials, it is necessary to increase their length, because this would result in better load transfers. According to Ashrafi and Hubert, one way to achieve this goal is through twisting of CNT, as in the case of textiles. The mechanical properties of polymers reinforced with twisted SWCNT arrays are determined in the presented method in this article by means of the Mori-Tanaka and a FE method. Small differences between the two methods are observed, with the FE method being the more accurate one. Furthermore, the authors observe a reduction in the Young’s modulus of the PNC as the twist angle increases. In addition, the effect of the SWCNT array orientation on the mechanical properties of the PNC is investigated in their article. The authors conclude that the Young’s modulus of the PNC is in general lower in the random distribution compared to the aligned case. Additionally, the dependence of the mechanical properties of the PNC on the aspect ratio of the twisted SWCNT arrays is also investigated in this article. Specifically, the authors show that twisting has a more pronounced effect on the computed values of the Young’s modulus of PNC for larger aspect ratios in the aligned case, while no significant influence is observed for the corresponding values in the random case. It is
further observed that the Young's modulus of PNC increases linearly as the volume fraction of SWCNT increases, for all values of aspect ratio. Finally, Ashrafi and Hubert compare the computed values for the Young's modulus with the values derived by Odegard et al. [73]. For both nanotube orientations (i.e. aligned and random) they find that the effect of twisting on the computed values is to decrease the value of the Young's modulus with respect to the Odegard's values.

Fisher et al. [23] also report a FE method which is capable of incorporating the effect of the nanotube's waviness on the mechanical properties of CNT. The computed properties are subsequently used in a Mori-Tanaka homogenization approach to determine the mechanical behavior of PNC. Figure 3.13 shows the three-dimensional FE model used to investigate the effect of waviness on the properties of CNT. The authors conclude, that the wavy nanotube has a Young's modulus which is significantly lower compared to the straight one. The Young's modulus of the curved nanotube is then used in the Mori-Tanaka method to determine the mechanical properties of PNC. Fisher et al. report that even for slightly wavy nanotubes, the values for the Young's modulus of the PNC computed by the proposed FE method are lower with respect to the Mori-Tanaka values in which straight nanotubes are assumed. However, a significant drawback of this method is that it considers a priori solid isotropic and perfectly bonded carbon nanotubes. Based on this assumption, the model proposed by Fisher et al. cannot distinguish any differences between SWCNT or MWCNT. In addition, the authors point out that their model is incapable of identifying the exact effect of nanotube waviness on the mechanical properties of PNC, since many
other parameters can be responsible for the discrepancies observed between experimental and modeling results.

![Diagram](image)

*Figure 3.13: The finite element model used to compute the mechanical properties of curved nanotubes. In this figure, "a" shows the amplitude of the assumed analytical form for the wavy nanotubes and "\( \lambda \)" denotes its wavelength.*

Finally, micromechanics methods, such as the previously mentioned Mori-Tanaka method, have also been used to determine the mechanical properties of PNC. For example, Seidel and Lagoudas [93] report a variety of micromechanics techniques that include a combination of methods capable of computing values for the important mechanical properties of PNC. Specifically, Seidel and Lagoudas use a composite cylinders method to first convert hollow nanotubes to equivalent solid ones and compute their mechanical properties, which are subsequently used both in self-consistent and Mori-Tanaka methods to provide esti-
mates for the mechanical properties of PNC. Both aligned and random distributions for the CNT in the polymers are used in this article. In the aligned case, the results derived by the micromechanics-type analysis are also compared to pertinent results from a FE method and are found in good agreement. The effects of interfaces and clustering on the mechanical properties of PNC are also investigated in this article. It is shown that the properties of the interfaces between the CNT and the polymer influence significantly the reinforcement of PNC, while the clustering effect is found to moderately improve only the transverse properties of the PNC. In the random case, the Mori-Tanaka method yields values for the Young’s modulus of the PNC which are compared to pertinent experimental results. In fact, the authors refer to some of the experimental results also used in this dissertation to validate the proposed model. However, the model of Seidel and Lagoudas provides values for the Young’s modulus of PNC which differ from the experimental results reported by Zhu et al. [127]. This discrepancy is rectified by the proposed model in this dissertation.

In addition, Shi et al. [95] also use the Mori-Tanaka method to examine the effect of wavy and agglomerated CNT on the mechanical properties of PNC. In particular, analytical expressions for the elastic parameters that determine the mechanical properties of two-phased composite media are provided in this article for both aligned and random orientations of the inclusion phases. These analytical formulas are subsequently utilized to investigate the influence of waviness on the mechanical properties of PNC. As reported by Shi et al., the effect of waviness is more pronounced in the case of aligned but curved carbon nanotubes. In this case both the moduli in the longitudinal and transverse direction
are affected by the parameters that characterize the waviness of CNT. However, in the case that the wavy carbon nanotubes are assumed to be randomly oriented in the polymer, there is no influence on the mechanical properties of PNC. Furthermore, Shi et al. investigate and show the importance of the effect of agglomerated CNT on the mechanical properties of PNC. In fact their model has been adapted and incorporated in the method presented in this dissertation, since it provides a straightforward procedure to include the effect of agglomeration of nanotubes in the Mori-Tanaka method. Therefore, a detailed description of the agglomeration model provided by Shi et al. is given in Chapter 4.
Chapter 4

The proposed Multiscale Stochastic Finite Elements Method (MSFEM)

This chapter presents the multiscale stochastic finite element method (MSFEM) proposed in this dissertation for determining mechanical properties of polymer nanocomposites (PNC) that consist of polymers reinforced with single-walled carbon nanotubes (SWCNT). Specifically, Chapter 4 describes the various models developed in the MSFEM to obtain specific information at different length scales, ranging from the nano- to the macroscale. Furthermore, this chapter provides, for completeness, the mathematical, physical and engineering background needed to explain and support the choices of the values of critical parameters that affect the determination of mechanical properties of PNC by the developed method.
4.1 PNC as random heterogeneous media

Chapters 2 and 3 of this dissertation present the structure and mechanical properties of SWCNT and PNC, respectively. In addition, Chapter 3 analyzes the experimental techniques used to measure the mechanical properties of PNC, and the various methods that have been suggested in the literature to model their mechanical behavior. It is, further, observed in Chapter 3 that experimentally measured values for the mechanical properties of PNC differ often from analytically and numerically computed ones. Based on this information, it is argued in Chapter 4 that PNC are solids that should be viewed as random heterogeneous media. The term “random” is used in the context of materials to denote random properties and uncertainties in the overall material behavior. Furthermore, the term “heterogeneous” describes the material structure and refers to the existence of heterogeneities that cause non-uniform effects, such as the ones modeled in this dissertation.

The proposed MSFEM identifies, models and quantifies the effect of randomly occurring structural heterogeneities on the mechanical properties of PNC. The method is based on images of actual structures of PNC at the nano-/microscales, and it develops a modeling strategy which incorporates information from the atomistic/molecular level to the microscale. Therefore, the “multiscale” nature of the proposed method is explained in this chapter by presenting the hierarchical use of information obtained at different length scales to reliably compute estimates for the mechanical properties of PNC that can be used for modeling in the macroscale. To this aim, the proposed method includes a sequence of computations and derivations that respect the “physics” of the problem and formulate an
efficient method for determining the mechanical behavior of PNC. Thus, it is argued in this
dissertation that the proposed method reflects reality because it investigates and models
the role of the spatial randomness in the structure of PNC in their mechanical properties,
which, it should be noted, has not been addressed yet in the pertinent literature. In addition,
the following chapters in this dissertation show that the proposed method is more generic
compared to other suggested models in the literature, since instead of attempting to repro-
duce the exact structure of PNC at the nano-microscales, it introduces a multiscale finite
element model which does not depend on detailed information about the actual morphology
of the reinforcement phase, yet it provides reliable results.

4.2 The proposed MSFEM

The proposed method for determining the mechanical properties of PNC is a multiscale
method composed of a series of models, as shown in Figure 4.1. This figure describes the
flow of information from the nano- to the microscale to compute estimates for mechanical
properties of PNC at the macroscale. The various models used and/or developed in the
proposed MSFEM to represent the structure and determine mechanical properties of PNC
are presented in this chapter by following the sequence shown in Figure 4.1.

4.2.1 MSFEM-Nanoscale

Polymer nanocomposites are nanomaterials and, therefore, their structure at the nanoscale
affects their macroscopic mechanical behavior. The various components in PNC are char-
Figure 4.1: The proposed multiscale stochastic finite elements method (MSFEM) for determining mechanical properties of PNC. Information obtained at the nanoscale is used in the microscale to compute estimates for the macroscopic mechanical behavior.
characterized by a wide range of length scales, which makes the modeling of this kind of nano-material challenging. Hence, nanoscale information is necessary to develop models that can determine mechanical properties of PNC accurately and reliably. Therefore, this section describes a modeling framework for PNC.

The first step in the proposed MSFEM is to identify a material region which can serve as a representative sample of the entire structure of PNC. This material region is subsequently used to identify and model uncertainties in the structure of PNC at the nanoscale.

### 4.2.1.1 Definition of a representative material region

The first step in determining mechanical properties of PNC by the proposed MSFEM is the choice of a material region (MR), similar to the representative volume element (RVE) used in solid mechanics. This material region is necessary for two reasons. First, it is a characteristic sample of the material under investigation, the structural morphology of which is observed and modeled. Second, the selected MR is the domain where mathematical formulations can be developed to determine mechanical properties of the macroscopic material.

The proposed method introduces a modeling strategy to fulfill these two goals for the case of random and heterogeneous PNC.

The concept of a RVE was initially defined by Hill [41] as a part of the solid that is, first of all, characteristic on average of the entire material. According to Hill's definition, the RVE is the smallest material region which is structurally typical of the entire solid, from a continuum point of view. Additionally, Hill points out that in the case of multiphase media
the RVE contains all phases in relative concentrations which reflect the overall material structure. Consequently, Hill states that a RVE, from a statistical point of view, is large enough to be representative of the overall material morphology.

In general, the definition of a RVE depends on the material under investigation. Specifically, Ostoja-Starzewski [77] suggests that the RVE is clearly defined only in two cases. The first involves materials with periodic structure, in which a “unit cell”, as it is frequently called, can be defined. For example, Figure 3.12 shows a unit cell used in the model developed by Song et al. [99] which is further assumed to be structurally typical of the entire structure. The second one includes a material volume which is large enough to contain a very large (mathematically infinite) set of “inclusions” which are uniformly dispersed. This material volume is equivalent to a homogeneous medium. It should be noted here that the term “inclusion” is used in solid mechanics to denote any distinct phase volume that is contained in the material.

In the case of random and heterogeneous media, in which there is no periodicity and/or uniformity in their structure, the choice of a material region (MR) that is characteristic of the entire medium depends on parameters, such as the number, size, shape, orientation, dispersion and spatial distribution of the inclusions. In addition, the size of the MR is usually a critical factor that determines the quality of the derived results. Specifically, it has been reported that the values for the mechanical properties of random heterogeneous media computed using certain MRs depend on their size, thereby creating a scale-effect [78, 102]. To overcome this scale-related problem, Ostoja-Starzewski [77] suggests a separation of
scales method to investigate the dependence of the material behavior on the size of the MR used. These scales are shown in Figure 4.2 and include the nano-/micro-scale and its characteristic length \( d \), the mesoscale which corresponds to the size of the selected MR \( L \), and finally the macroscale which includes the dimensions of the entire solid.

![Figure 4.2: The separation of scales proposed by Ostoja-Starzewski [77]. The size of the inclusions at the nano-/micro-scale is determined by \( d \), while \( L \) denotes the dimensions of the material region selected to investigate the mechanical behavior of the solid.](image)

The separation of scales shown in Figure 4.2 quantifies the scale effect observed when determining the mechanical behavior of solids. Specifically, as the fraction of the characteristic length \( L \) over the typical dimension of the inclusion \( d \) tends to infinity, the MR is asymptotically equal to a RVE. Hence, for any finite value of this fraction, one should examine the scale effect on the computed results, as shown in this dissertation.

The proposed MSFEM yields values for the mechanical properties of PNC based on the MR defined in Figure 4.3. Examining, Figure 4.3, it can be seen that the MR used in the proposed method corresponds to a portion of a cross-section of the macroscopic PNC. The
selected MR is actually equal to the size of typical scanning electron microscope (SEM) images of the structures of PNC reported in the literature. Therefore, the selected MR is defined at the nanoscale by relying on information about the actual structure of PNC at that scale. Furthermore, the proposed method in this dissertation uses this information and develops a computational method to investigate the effect of the structure of PNC on the computed values for their mechanical properties.

Figure 4.3: The material region (MR) used in the proposed method as a reference area which is typical of the entire structure of PNC. The selected MR corresponds to the size of images of actual structures of PNC. In this MR, a multiscale stochastic finite element method is developed for determining the mechanical properties of PNC.
4.2.1.2 Spatial randomness identification

Section 3.2.3 of this dissertation presented experimental and characterization evidence for the shape, orientation distribution and size of the inclusion phases in PNC. The existence of heterogeneities in the structure of PNC, such as SWCNT bundles, clusters and agglomerates induces a sort of spatial randomness, which has not been taken into account in suggested models in the literature for determining the mechanical behavior of PNC. However, this kind of randomness has been the focus of several studies in the area of probabilistic engineering mechanics. For example, the book by Ghanem and Spanos [29] and the article by Graham and Baxter [35] present models for the randomness observed in the mechanical properties of materials and structures.

The proposed MSFEM relies on the premise that the non-uniform dispersion of SWCNT in polymers causes variations in the local mechanical properties of PNC which need to be modeled to reliably determine the overall mechanical behavior. To this aim, the proposed method models the SWCNT dispersion in PNC using information obtained by observing actual images of the structure of PNC and by developing an appropriately defined random field model.

Specifically, Figure 4.4 presents an SEM image of one of the PNC modeled in this dissertation [93] and an illustration of the way the proposed MSFEM identifies randomness in the nanoscale. Based on Figure 4.4, it can be concluded that the SWCNT dispersion in polymers presents significant local variations, which are represented by the different color intensities in this image, in which darker areas correspond to higher concentrations
Figure 4.4: An actual image of a polymer nanocomposite is the material region (MR) used for modeling purposes in the proposed MSFEM. A grid of material points is selected based on this choice of MR, and in each point a random value for the local volume fraction is assigned to represent areas with higher (darker regions in the image) and lower (lighter regions in the image) concentration of SWCNT.

of SWCNT. Since the MR used in the proposed MSFEM is considered to be characteristic of the entire material, the relative concentrations of SWCNT in a SEM image of the PNC are statistically equivalent to the total amount of nanotubes in it. The number of SWCNT in the polymer matrix is quantified using the notion of the volume fraction defined in Equation 4.1.

\[ v = v_{SWCNT} + v_{polymer} = 1 \]  \hspace{1cm} (4.1)

where \( v_{polymer} \) is the polymer volume fraction and \( v_{SWCNT} \) is the SWCNT one, defined in Equation 4.2

\[ v_{SWCNT} = \frac{V^S}{V} \]  \hspace{1cm} (4.2)

In Equation 4.2, \( V^S \) is the volume occupied by the SWCNT and \( V \) is the total volume of
the PNC.

Therefore, the local volume fraction in the selected material points of the MR used in the proposed MSFEM quantifies the observed variations in the spatial dispersion of SWCNT in polymers. The values of the local SWCNT volume fractions and the number of selected material points are two of the parameters in the proposed method which affect heavily the derived results for the mechanical properties of PNC and, therefore, their role is explained in the following sections of this chapter.

4.2.1.3 Random field modeling

The proposed MSFEM quantifies the spatial dispersion of SWCNT in polymers by the procedure described in section 4.2.1.2 and by using the random field model presented in this section. For completeness, some background information on probability theory and random process is also included in this section. A detailed description of the pertinent mathematical fields is provided in books available in the literature [38, 80].

Probability theory background

A sample space $\Theta$ is the collection of all possible results of "experiments" in which there is no a priori information about the observed outcome. An example of this kind of experiment is the rolling of a die, in which case $\Theta = \{1, 2, 3, 4, 5, 6\}$. In general, any outcome of these "random trials" is called an "event", which belongs in $\Theta$ and is referred as $\theta$. A random variable (RV) $x$ is a mapping of an event from the sample space $\Theta$ to the set of real numbers $\mathbb{R}$. Therefore, in the same example of rolling a die, a RV can be used to represent
numerically an event, such as the sum of the numbers observed when rolling the die three times. Each RV has a cumulative distribution function (CDF), defined in Equation 4.3 and a probability density function (PDF), which is always positive and related to the CDF, as shown in Equation 4.4.

\[
F(x) = \mathbb{P}(X \leq x) \quad \text{where} \quad x \in \mathbb{R} \tag{4.3}
\]

\[
F(x) = \int_{-\infty}^{x} f(u)du \quad \text{where} \quad x \in \mathbb{R} \tag{4.4}
\]

In Equation 4.3, the symbol \( \mathbb{P} \) denotes "probability". Hence, the CDF expresses the "probability of occurrence" of an event, which is a number between 0 and 1. Moreover, the function \( f(x) \) in Equation 4.4 is the PDF of the RV.

A RV can be further statistically described by its moments, such as the mean or expected value and the variance, defined in Equations 4.5 and 4.6, respectively. In these equations the expectation symbol \( \mathbb{E} \) is used.

\[
\mu = \mathbb{E}[x] = \int_{-\infty}^{\infty} xf(x)dx \tag{4.5}
\]

\[
\sigma^2 = \mathbb{E}[(X - \mu)^2] = \int_{-\infty}^{\infty} (x - \mu)^2 f(x)dx \tag{4.6}
\]

Furthermore, it should be noted that two RVs \( x \) and \( y \) are "independent", if

\[
f_{xy}(x, y) = f_x(x)f_y(y), \quad \text{for all} \quad x, y \in \mathbb{R} \tag{4.7}
\]

and "orthogonal," if

\[
\mathbb{E}[xy] = 0 \tag{4.8}
\]
A random process (RP) $X_t, t \in T$, or simply $X(t)$ is a collection of indexed RVs. This index could be discrete or continuous, resulting in discrete and continuous RPs, respectively. Figure 4.5 shows an example of $n$ realizations of a continuous RP, for which the index set is time, $t$. A RP is completely defined in the case that the joined PDF (or CDF) of all its RV is known. If the joint statistics of the RVs that form a RP are not known, information about the RP is obtained by its mean value, covariance function, autocorrelation

Figure 4.5: An example of a continuous random process (RP). The RP is a collection of random values in time. Each "time series" shown in the figure is a realization of the random process. For each instant of time, e.g. $t_1$, the values observed in all realizations are described by a random variable.
function and power spectrum defined in Equations 4.9, 4.10, 4.11, and 4.12, respectively.

\[ \mu(t) = E[X(t)] \quad (4.9) \]

\[ Cov(t_1, t_2) = E\{[X(t_1) - \mu(t_1)][X(t_2) - \mu(t_2)]\} \quad (4.10) \]

\[ R(t_1, t_2) = E[X(t_1)X(t_2)] \quad (4.11) \]

\[ P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} R(\tau) \exp(i\omega\tau) d\tau \quad (4.12) \]

Two important concepts related to RP are stationarity and ergodicity. A RP is strictly stationary if its joined PDF (or CDF) is not affected by a shift in the indexed set, e.g., time. The RP is weakly (wide sense) stationary if its mean value remains constant for a similar shift in the indexed set, while its covariance function depends only on the difference between two values of the indexed set. Furthermore, the RP is ergodic when averages over all realizations (also called “ensemble averages”) can be replaced by “sample averages” made in a single realization of the RP. In practical applications, the ergodicity assumption is necessary in cases in which only one realization of a stationary RP is available.

A random field (RF) is a generalization of a RP in higher dimensions [109]. If \( S(x) \) is a RF, then \( x \) could be a point or a vector in \( \mathbb{R}^d \), in which cases the RF is called “univariate” and “multivariate,” respectively. In addition, a RF could be “one-dimensional” (for \( d = 1 \)) or “multidimensional” (for \( d > 1 \)). An example of a univariate, one-dimensional RF is the time-series shown in Figure 4.5. Moreover, it is noted that the RFs used in this dissertation to model the spatially varying properties of PNC are continuous univariate and two-dimensional.
The statistics defined in Equations 4.9, 4.10, 4.11, and 4.12 are also used to describe a RF by taking into account its multidimensional nature. In addition, the concept of stationarity can be extended in higher dimensions, in which case it is called homogeneity. Therefore, a RF is homogeneous, if its mean value is constant and its covariance or, equivalently, its correlation function depends only on the difference between two positions in \( \mathbb{R}^d \).

Similarly, ergodicity assumptions are also made in the case that limited samples of RFs are available.

Random fields used in practical applications are often "discretized". This means that a continuous multidimensional RF is represented by means of a finite set of RVs grouped in a random vector \( \mathbf{X} \), written as

\[
\{x_k, k = 1, \ldots, n\}
\]

Many discretization schemes have been suggested in the literature. The articles by Li and Der Kiureghian [55] and Zeldin and Spanos [123] present and compare some of the most popular discretization schemes which are often used in stochastic finite elements applications.

Finally one of the most important issues in using RFs for modeling purposes is the generation of sample realizations. To this aim, Spanos and Zeldin [100] present an overview of some of the methods used in numerical applications. Moreover, one of the reported methods for digital generation of RF samples is the one introduced by Shinozuka and Deodatis [97]. This method is used in Chapter 6 and, therefore, is presented next.

Shinozuka and Deodatis propose a spectral representation method to simulate univariate
two-dimensional homogeneous RFs $S(x)$ that have mean value equal to zero and real, positive and symmetric power spectrum, defined in Equation 4.14

$$P_{SS}(k_x, k_y) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R_{SS}(x_n, y_n) e^{-i(k_xx_n+k_yy_n)} dx_n dy_n$$  \hspace{1cm} (4.14)

where $k_x$ and $k_y$ are frequencies corresponding to the two dimensions $x$ and $y$, and $x_n, y_n$ are the coordinates of a two-dimensional grid of points.

This type of RF, according to Shinozuka and Deodatis, can be simulated by the series shown in Equation 4.15, in which the fast Fourier transform (FFT) technique is used in order to take advantage of its efficiency in digital simulations.

$$f^i(p\Delta x_n, q\Delta y_n) = Re \sum_{g=0}^{N_x-1} \sum_{h=0}^{N_y-1} B_{gh} \exp \left[ i(g\Delta \kappa_x)(p\Delta x_n) + i(h\Delta \kappa_y)(q\Delta y_n) \right] +$$

$$\tilde{B}_{gh} \exp \left[ i(g\Delta \kappa_x)(p\Delta x_n) - i(h\Delta \kappa_y)(q\Delta y_n) \right]$$  \hspace{1cm} (4.15)

where $p = 0, 1, \ldots, N_x - 1$ and $q = 0, 1, \ldots, N_y - 1$. In Equation 4.15, $N_x$ and $N_y$ are number of points in the $x$ and $y$ axis, respectively. Moreover, the symbol $Re$ denotes the real part of an imaginary number and $\Delta x_n, \Delta y_n$ are equal to the spacing between points in the $x$ and $y$ axis, respectively. The coefficients $B_{gh}$ and $\tilde{B}_{gh}$ are defined in Equations 4.16 and 4.17.

$$B_{gh} = \sqrt{2} A_{gh} \exp[i\phi_{gh}^{(1)(i)}]$$  \hspace{1cm} (4.16)

$$\tilde{B}_{gh} = \sqrt{2} \tilde{A}_{gh} \exp[i\phi_{gh}^{(2)(i)}]$$  \hspace{1cm} (4.17)

where $\phi_{gh}^{(1)(i)}$, $\phi_{gh}^{(2)(i)}$ are independent random phase angles distributed over the interval
and the coefficients $A_{gh}$ and $\tilde{A}_{gh}$ are equal to

$$A_{gh} = \sqrt{2P_{SS}(\kappa_{g}, \kappa_{h})\Delta \kappa_{x} \Delta \kappa_{y}}$$ (4.18)

$$\tilde{A}_{gh} = \sqrt{2P_{SS}(\kappa_{g}, -\kappa_{h})\Delta \kappa_{x} \Delta \kappa_{y}}.$$ (4.19)

In Equations 4.18 and 4.19,

$$\kappa_{xg} = g\Delta \kappa_{x}$$ (4.20)

$$\kappa_{yh} = h\Delta \kappa_{y}$$ (4.21)

and

$$\Delta \kappa_{x} = \frac{\kappa_{x_{max}}}{M_{x}}$$ (4.22)

$$\Delta \kappa_{y} = \frac{\kappa_{y_{max}}}{M_{y}}$$ (4.23)

where $M_{x}$ and $M_{y}$ denote the number of points for each axis in the frequency domain.

Furthermore, $\kappa_{x_{max}}$ and $\kappa_{y_{max}}$ are the maximum frequency values in the two axes.

In addition, Shinozuka and Deodatis propose the following constraints in order to derive accurate results:

$$A_{0h} = A_{g0} = 0 \text{ for } g = 0, 1, \ldots, N_{x} - 1 \text{ and } h = 0, 1, \ldots, N_{y} - 1$$ (4.24)

$$\Delta x_{n} \leq \frac{2\pi}{2\kappa_{x_{max}}}; \Delta y_{n} \leq \frac{2\pi}{2\kappa_{y_{max}}}$$ (4.25)

$$N_{x} \geq 2M_{x}; N_{y} \geq 2M_{y}$$ (4.26)
The proposed random field model

The proposed random field model in the MSFEM presented in this dissertation quantifies the spatial randomness observed in the SWCNT dispersion in polymers. Examining Figure 4.4, it can be concluded that a value for the local SWCNT volume fraction is sought for every material point defined in the MR. These values in the proposed model are assumed to be RVs that have specific PDFs. Specifically, a variety of PDFs including the uniform, beta and lognormal distributions shown in Equations 4.27, 4.28 and 4.29 are used, since no a priori information on the dispersion properties of SWCNT in polymers is taken into account.

\[ f(x) = \begin{cases} \frac{1}{b-a}, & a < x < b \\ \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)}x^{a-1}(1-x)^{b-1}, & 0 < x < 1, \quad a > 0, \quad b > 0 \\ \frac{1}{x\sqrt{2\pi\sigma^2}}e^{-\frac{(\ln x-\mu)^2}{2\sigma^2}}, & x \geq 0 \end{cases} \]  

(Equations 4.27, 4.28, 4.29)

The mean value in these PDFs is set always equal to the SWCNT volume fraction determined by using the available experimental information on the exact weight percentage of nanotubes in the polymer. Additionally, the variance in the PDFs is chosen based on the fact that the values for the SWCNT volume fraction cannot be negative or larger than 1. Chapter 5 presents samples of random vectors with RVs that have the three PDFs defined in Equations 4.27, 4.28 and 4.29, respectively. The effect of the choice of the PDF on the computed values for the mechanical properties of PNC is also investigated in Chapter 5.

The random vectors obtained by assuming that the SWCNT volume fractions in PNC can be represented by RVs that have specific PDFs are, further, assumed to be discretiza-
tions of some continuous, univariate, two-dimensional and homogeneous RFs. Therefore, if \( S(x) \) denotes the RF of the local SWCNT volume fractions in PNC, then the generated random vectors are the set of the RF values at locations in \( \mathbb{R}^2 \) that coincide with the selected material points in the MR. Hence,

\[
S(x) \xrightarrow{\text{Discretization}} S_N^i
\]

where,

\[
S_N^i = S(x_n, y_n)
\]

(4.30)

In Equation 4.30, \( S_N^i \) is the i-th sample of a random vector which represents the discretized RF in a grid of \( n \times n = N \) points.

Based on the ergodicity assumption, the sample statistics of the generated random vectors can be computed. Therefore, Equations 4.31, 4.32 and 4.33 present the mean value, variance and power spectrum of the discretized RF. Hence,

\[
\mu_S = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \frac{S(x_n, y_n)}{N_x N_y}
\]

(4.31)

\[
\sigma^2_S = \frac{1}{N_x N_y - 1} \left( \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} S(x_n, y_n)^2 - \left( \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} S(x_n, y_n) \right)^2 \right)
\]

(4.32)

where \( N_x \) and \( N_y \) are the number of grid points in the \( x \) and \( y \) directions, respectively, and

\[
P_{SS}(k_x, k_y) = \frac{1}{N_x N_y \Delta x \Delta y} \left| \Delta x \Delta y \sum_{p=1}^{N_x-1} \sum_{q=1}^{N_y-1} S(x) \exp \left[ -\frac{2i\pi k p}{N_x} - \frac{2i\pi m q}{N_y} \right] \right|^2.
\]

(4.33)

In Equation 4.33,
\[ k = \left\{ \frac{(N_x - 1)}{2}, \frac{(N_x - 1)}{2} + 1, ..., 0, ..., \frac{(N_x - 1)}{2} - 1, \frac{(N_x - 1)}{2} \right\} \]

\[ m = \left\{ \frac{(N_y - 1)}{2}, \frac{(N_y - 1)}{2} + 1, ..., 0, ..., \frac{(N_y - 1)}{2} - 1, \frac{(N_y - 1)}{2} \right\} \]

are the coordinates of the selected grid of points in the MR, while \( k_x = 2\pi k \) and \( k_y = 2\pi m \) are the corresponding frequencies for which power spectrum values are computed.

### 4.2.2 MSFEM-Microscale

Section 4.2.1 of this chapter presents the information obtained at the nanoscale about the structure of PNC. Therefore, the non-uniform spatial distribution of SWCNT in polymers is quantified and modeled in the proposed MSFEM by using a random field model, in which the local SWCNT volume fraction values are represented by appropriately defined random numbers. Furthermore, this information is used as an input for modeling of the structure and mechanical properties of PNC at the microscale. In general, this transition in terms of length scales is accomplished by means of some “homogenization” technique.

Materials homogenization is performed in micromechanics-type analyses, in which the original heterogeneous material is replaced by an equivalent homogeneous one, under appropriate assumptions and conditions. This homogenization is useful since it is easier to compute mechanical properties for a single-phase than a multi-phase material. Therefore, the proposed MSFEM incorporates the models developed at the nanoscale to develop a micromechanics model capable of homogenizing PNC. In particular, the MSFEM models the microscale heterogeneities in the structure of PNC and, furthermore, computes values for the local mechanical properties of PNC at the microscale which are subsequently used to
determine the overall mechanical behavior of PNC.

4.2.2.1 Quantify Agglomeration

Section 3.2.3 of this dissertation examines the inclusion phases in PNC and cites a number of references that, based on experimental evidence, report the existence of SWCNT bundles, clusters and agglomerates. However, many of the proposed methods in the pertinent literature for determining the mechanical properties of PNC do not take into account the existence of agglomerated SWCNT in polymers and make some simplifying assumptions about the PNC structure at the microscale (see section 3.2.5). Nevertheless, Shi et al. [95] investigate the effect of the agglomeration of SWCNT in polymers on the mechanical properties of PNC using a micromechanics-type homogenization method. Their model is used in the proposed MSFEM to examine the role of SWCNT agglomerates on the computed values for the local mechanical properties of PNC.

Figure 4.6 shows an example of the structure of PNC at the microscale. It can be seen in this figure that at this length scale SWCNT tend to agglomerate in the form of irregularly shaped clusters, appearing as the darker areas in the image. Therefore, for modeling purposes it is important to determine the shape, concentration and mechanical properties of these agglomerates to realistically model the structure of PNC at the microscale. To this aim, based on the model presented by Shi et al. [95] and the information provided in section 3.2.3, the microscale morphology of PNC in the proposed MSFEM is modeled as shown in Figure 4.7.
Figure 4.6: An example of the structure of PNC at the microscale. The darker areas in this image are SWCNT agglomerates of various shapes and sizes [45].

Figure 4.7: The model structure of PNC assumed in the proposed MSFEM. Carbon nanotubes are partially dispersed in the matrix and, therefore, a hybrid matrix is contained in a specific volume \( V \) of the PNC. In addition, the nanotubes are agglomerated in spherical inclusions, as it is shown in this figure. The inclusions consist of both polymer and carbon nanotubes.
Based on Figure 4.7, a finite volume $V$ of the PNC comprises a modified matrix and spherical inclusions. Therefore,

$$V = V^{\text{matrix}} + V^{\text{inclusions}}$$  \hspace{1cm} (4.34)

where $V^{\text{matrix}}$ and $V^{\text{inclusions}}$ are the volumes occupied by the modified matrix and inclusions, respectively. In the material model shown in Figure 4.7 the degree of agglomeration of SWCNT in the PNC structure can be quantified by using the agglomeration index $\xi$ defined in Equation 4.35.

$$\xi = \frac{V^{\text{inclusion}}}{V}.$$  \hspace{1cm} (4.35)

From the definition of $\xi$ in Equation 4.35 it can be concluded that the closer to 1 the agglomeration index is, the more homogeneous the PNC becomes.

Furthermore, both phases in $V$ consist of polymer reinforced with perfectly bonded, straight, finite, randomly oriented and homogeneously dispersed SWCNT. Hence in the proposed MSFEM, if $V^C$ is the volume occupied by SWCNT, then

$$V^C = V^{C^{\text{matrix}}} + V^{C^{\text{inclusions}}}$$  \hspace{1cm} (4.36)

where $V^{C^{\text{matrix}}}$ and $V^{C^{\text{inclusions}}}$ are the SWCNT volumes in the modified matrix and spherical inclusions, respectively. Based on Equation 4.36 the MSFEM quantifies the amount of SWCNT in each phase by using the dispersion index defined in Equation 4.37.
\[ \zeta = \frac{V_{\text{inclusions}}^C}{V^C} \]  

(4.37)

According to the definition in Equation 4.37, the closer to 0 the dispersion index is, the more homogeneous the PNC becomes. In addition, if \( v^C \) is the total SWCNT volume fraction defined in Equation 4.38

\[ v^C = \frac{V^C}{V} \]  

(4.38)

then

\[ v^C = v_{\text{matrix}}^{SWCNT} + v_{\text{inclusion}}^{SWCNT} \]  

(4.39)

where \( v_{\text{matrix}}^{SWCNT} \) and \( v_{\text{inclusion}}^{SWCNT} \) are the corresponding SWCNT volume fractions in \( V_{\text{matrix}}^C \) and \( V_{\text{inclusions}}^C \), respectively.

The proposed MSFEM investigates the effect of the agglomeration and dispersion of SWCNT in polymers in the mechanical properties of PNC by computing values for the mechanical properties of the inclusions, the hybrid matrix and the two-phase PNC. These computations are made using the Mori-Tanaka micromechanics method, which is analyzed in the following section, and a stochastic finite element scheme that is presented later in this chapter.
4.2.2.2 Micromechanics homogenization

Background

The analysis of materials with heterogeneous structure is greatly facilitated when the original material that consists of two or more phases is replaced with an equivalent homogeneous material. The main objective in materials homogenization is to determine the mechanical properties of the homogeneous material, which are usually called “effective” to point out their difference from the actual properties of the heterogeneous material.

Figure 4.8 presents schematically the homogenization of a heterogeneous material. To this aim, based on section 4.2.1.1 a representative volume element (RVE) is considered, which has a finite volume \( V \) and is bounded by the surface \( \partial V \). The RVE comprises a matrix and a single microscale inclusion with volume \( V^{in} \). Both phases are assumed to be linearly elastic, homogeneous, but not necessarily isotropic and perfectly bonded. No further assumptions regarding the shape and orientation of the inclusion are made at this point. For a detailed description of the concepts that appear in the analysis of this section, some references available in the literature are recommended. Hence, the book by Boriesi and Chong [10] is suggested for elasticity concepts, the book by Kollar and Springer [50] for an analysis of the anisotropic behavior of materials and the book by Nemat-Nasser and Hori [71] for micromechanics of heterogeneous media.

In the following analysis, bold face letters are used to denote tensors and vectors. To determine the effective mechanical properties of the equivalent homogeneous RVE shown in Figure 4.8, a uniform strain \( \varepsilon^S \) is applied on \( \partial V \). In this case, the linear surface displace-
Figure 4.8: The homogenization of a heterogeneous RVE having finite volume $V$ and consisting of a matrix and an inclusion phase. In materials homogenization the original heterogeneous structure is replaced by an equivalent homogeneous one.

Elongations in the RVE are

$$u^S = \varepsilon^S x \text{ on } \partial V \quad (4.40)$$

where $x$ is a position vector which is relative to a Cartesian coordinate system. If the RVE considered had no inclusion, then the strain field (as well as the corresponding stress field) in it would be uniform, as shown in Equation 4.41

$$\varepsilon^S \equiv \varepsilon^{RVE} = C\sigma^{RVE} \quad (4.41)$$

where $C$ is the material’s compliance tensor and $\sigma$ denotes the stress tensor. However, the presence of the inclusions causes perturbations in the uniform strain field defined in Equation 4.41. Hence, the strains in the heterogeneous RVE are equal to

$$\varepsilon^{RVE} = \varepsilon^S + \varepsilon^D \quad (4.42)$$
where $\epsilon^D$ denotes the strains caused by the inclusion. In this case, the strains and stresses in the matrix and inclusion phases are shown in Equations 4.43 and 4.44, respectively.

$$\epsilon^{RVE} = C^m(\sigma^S + \sigma^D) \quad \text{in} \quad V - V^{in} \quad \text{(4.43)}$$

$$\epsilon^{RVE} = C^{in}(\sigma^S + \sigma^D) \quad \text{in} \quad V^{in} \quad \text{(4.44)}$$

In Equations 4.43 and 4.44, $C^m$ and $C^{in}$ are the compliance tensors of the matrix and the inclusion phases, respectively. To homogenize the heterogeneous RVE, a strain field $\epsilon^H$ can be theoretically applied on the inclusion to make strains uniform in $V$. This homogenization strain is called “eigenstrain” and is related to the perturbation strains caused by the inclusion, by means of an integral operator [71]. Eshelby [20] showed that in the case that the matrix is infinitely extended and contains a single inclusion which has an ellipsoidal shape, the perturbation strain is related to the eigenstrain, as shown in Equation 4.45.

$$\epsilon^D = S^{in} \epsilon^H \quad \text{(4.45)}$$

where $S^{in}$ is a fourth-order tensor called “Eshelby’s tensor”, which has symmetries (see [71]), is independent of the mechanical properties of the inclusion. In the case that the matrix is isotropic Eshelby’s tensor is completely defined by the aspect ratio of the inclusion and the mechanical properties of the matrix.

Many methods have been suggested for determining the mechanical properties of heterogeneous media that take into consideration the homogenization procedure presented in this section. One of the most successful ones is the Mori-Tanaka method which is directly based on Eshelby’s result shown in Equation 4.45 and has been applied in a variety of
micromechanics problems [6, 71].

The Mori-Tanaka method

The Mori-Tanaka (MT) method can be used to determine the effective mechanical properties of composite materials. To this aim, the formulation developed by Benveniste [6] is used in this section to explain the incorporation of the MT method in the proposed MSFEM.

The general two-phase composite shown in Figure 4.9 is considered. The composite consists of a matrix and an inclusion phase which comprises a number of ellipsoidal particles. The indices "1" and "2" are used to denote the matrix and inclusion phase, respectively. The only assumptions made at this point are: perfect bonding between the two phases and elastic anisotropic behavior. Let the boundary conditions defined in Equation 4.40 be applied on the surface $\partial V$ of the volume $V$ of the composite. In this case, the average strains in the composite include the contribution of both phases and can be expressed as

$$\bar{\varepsilon} = v_1 \bar{\varepsilon}^1 + v_2 \{ \bar{\varepsilon}^2 \}$$  \hspace{1cm} (4.46)

where $v$ denotes volume fraction, the bar over the strains is used to refer to average strains in the composite and the curly brackets designate averaging over all possible orientations. Therefore, the strains and stresses in the composite are

$$\bar{\varepsilon} = C^{eff} \bar{\sigma}$$  \hspace{1cm} (4.47)
Figure 4.9: The RVE considered in the formulation of the Mori-Tanaka method presented in section 4.2.2.2. The composite material is assumed to comprise a matrix and inclusion phase which consists of a number of ellipsoidal particles.

\[ \sigma = T^{\text{eff}} \varepsilon \]  \hspace{1cm} (4.48)

where \( C^{\text{eff}} \) and \( T^{\text{eff}} \) are the effective compliance and stiffness tensors of the composite, which according to the MT method can be expressed as

\[ C^{\text{eff}} = C_1 + \nu_2 \left[ (C_2 - C_1) A \right] \left[ \nu_1 I + \nu_2 \{ A \} \right]^{-1} \]  \hspace{1cm} (4.49)

\[ T^{\text{eff}} = T_1 + \nu_2 \left[ (T_2 - T_1) B \right] \left[ \nu_1 I + \nu_2 \{ B \} \right]^{-1} \]  \hspace{1cm} (4.50)

respectively. In Equation 4.49, \( A \) is a orientation dependent tensor that relates the stresses in the two phases, as shown in Equation 4.51
\[ \sigma^2 = A\sigma^1. \]

Furthermore, \( A \) is related to the compliance tensor of the matrix and the stiffness tensor of the inclusion. Thus,

\[ A = T_2 B C_1 \]

where \( B \) is another orientation dependent tensor which is defined as

\[ B = [I + ST_1^{-1}(T_2 - T_1)]^{-1} \]

and relates the strains in the matrix and the inclusion phases of the composite. Hence,

\[ \varepsilon^2 = B\varepsilon^1. \]

In Equation 4.53, \( S \) is Eshelby's tensor defined in Equation 4.45.

Therefore, based on Equations 4.49 and 4.50 it can be concluded that to determine the effective mechanical properties of two-phase composites using the MT method, the compliance or stiffness tensors and the volume fractions of the constituent phases, as well as Eshelby's tensor are needed. The way these parameters are determined by the proposed MSFEM is analyzed next.

The PNC in the proposed MSFEM are modeled as two-phase media consisting of a hybrid matrix and spherical inclusions, as presented in section 4.2.2.1. Both phases consist of polymer and SWCNT which are further assumed to be perfectly randomly oriented. In addition, as described in section 3.2.5 the model by Odegard et al. [73] is used in the
proposed method to convert the hollow SWCNT into equivalent solid fibers that can be used in micromechanics analyses.

The first step in the application of MT method in the MSFEM is the determination of the mechanical properties of the polymers and the SWCNT. To this aim, polymers are assumed to be isotropic and consequently, the polymer stiffness tensor is characterized by two independent elastic parameters; the Young's modulus and the Poisson ratio. These constants are determined by the experimental results available in the literature and presented in Chapter 5 of this dissertation. In the case of SWCNT, the model by Odegard et al. results in transversely isotropic equivalent solid fibers. Therefore, five independent elastic parameters are determined. The values for the elastic parameters that determine the mechanical properties of the solid fibers used in the proposed MSFEM are presented in Table 4.1. In Table 4.1, $E_{11}$ and $E_{22}$ are the longitudinal and transverse moduli, respectively, $v_{12}$ is the primary Poisson ratio and $G_{12}$, $G_{23}$ are the shear moduli in the planes defined by the axis 1-2 and 2-3 (see Figure 3.11).

The second step in the MT method used in the proposed MSFEM is the determination of the volume fractions of the two phases in the composite material. Specifically, the MSFEM presented in this dissertation computes values for the SWCNT volume fraction based on the procedure analyzed in sections 4.2.1.2 and 4.2.1.3 of this chapter. Moreover, it should be noted that in fabrication procedures, the number of SWCNT in polymers is quantified by the use of the weight percentage defined in Equation 4.55 [82].
Table 4.1: The five independent elastic parameters of the equivalent solid fibers used in the micromechanics homogenization of the PNC by the proposed MSFEM

<table>
<thead>
<tr>
<th>Elastic Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{11}(\text{GPa})$</td>
<td>450.47</td>
</tr>
<tr>
<td>$E_{22}(\text{GPa})$</td>
<td>12.13</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>0.42</td>
</tr>
<tr>
<td>$G_{12}(\text{GPa})$</td>
<td>27</td>
</tr>
<tr>
<td>$G_{23}(\text{GPa})$</td>
<td>4.40</td>
</tr>
</tbody>
</table>

\[ w_{SWCNT} = \frac{\text{SWCNT weight}}{\text{polymer weight}} \times 100\% \quad (4.55) \]

To determine the average volume fraction of SWCNT in PNC, Equation 4.56 is used in the proposed MSFEM.

\[ v = \frac{w_S \rho_P}{w_S \rho_P + (1 - w_S) \rho_S} \quad (4.56) \]

In Equation 4.56 the indices “S” and “P” denote SWCNT and polymer, respectively, while \( \rho \) is a symbol for density. Values for the polymer and SWCNT densities are presented in Chapter 5.

Finally, the third step in the MT method used in the proposed MSFEM is the determination of the Eshelby tensor. At this point it should be noted that the MT method is used in the MSFEM to compute the mechanical properties of (i) the SWCNT reinforced polymer
(i.e. hybrid matrix), (ii) the spherical inclusions and (iii) the two-phase PNC consisting of the hybrid matrix and the spherical inclusions. In cases (i) and (ii) the reinforcement phase consists of perfectly bonded, straight and randomly oriented SWCNT. To determine the Eshelby tensor in this case, the article by Qiu and Weng [85] is used and the Eshelby tensor determined corresponds to this particular shape of the reinforcement phase. Moreover, Qiu and Weng provide the Eshelby tensor for spherical inclusions in a matrix which corresponds to the previously mentioned case (iii). In general, the only inputs required to use the expressions for the Eshelby tensors presented in [85] are the Poisson ratio of the matrix and the aspect ratio of the inclusions. In Chapter 5, experimentally determined values for the Poisson ratio of the polymers used in the proposed method are provided. In addition, pertinent assumptions are made about the aspect ratios of the SWCNT based on experimental evidence.

4.2.2.3 Monte Carlo finite elements method

The proposed method in this dissertation for determining the mechanical properties of PNC is a finite elements (FE) method with many additional components added and integrated into a multiscale stochastic FE representation of the continuum problem under consideration. Values for the mechanical properties are computed in the proposed method by solving a two-dimensional elasticity problem using a FE discretization/representation, in which many of the included parameters and the overall procedure incorporates information obtained at different length scales. Hence, this section presents the stochastic finite elements
part of the proposed multiscale method used for modeling the mechanical properties of PNC.

Deterministic finite elements background

Finite elements methods (FEM) are commonly used in modern engineering to solve a variety of problems, such as the determination of stress, strain, heat and electrical fields in materials and structures [2, 128]. In general, FEM are based on the idea of decomposing a complex physical domain into a finite number of smaller regions called “elements,” for which an approximate solution can be derived using certain mathematical principles. Figure 4.10 shows the basic steps typically followed in FEM.

In principle, modeling of complex geometries of materials and structures is often easier in the case that the considered continuum is discretized. The mathematical formulation for this kind of discretization results in some governing differential equation, such as the one shown in Equation 4.57.

\[ \mathbb{D}u = F \]  

(4.57)

In Equation 4.57, \( \mathbb{D} \) denotes the differential operator that acts on an unknown function \( u \) that describes the domain (e.g., displacements field) and \( F \) describes the externally applied generalized “loads” on the system, for example forces, displacements, heat, etc. Many mathematical methods have been suggested to solve Equation 4.57. However, in FEM weighted residual and variational formulations are usually used.

To explain the solution procedure followed in FEM, the weighted residual method is
used [2]. Therefore, an approximate solution $\tilde{u}$ to the governing Equation 4.57 is assumed. This approximation is of the form shown in Equation 4.58

$$u(x) \approx \tilde{u}(x) = \sum_{i} N_i(x)a_i$$ (4.58)

where $N$ are functions of the position vector $x \in \mathbb{R}^d$ and $a$ is a vector of values of $u$ in specific locations in the domain. Since $\tilde{u}$ is an approximation of $u$, then

$$\mathbb{D}(\tilde{u}) - F = R \neq 0$$ (4.59)
Hence, the approximation defined in Equation 4.58 creates a residual $R$ to Equation 4.57, after substitution. To this aim, the weighted integral of Equation 4.60 can be used to force the residual to zero.

$$I = \int_{\Omega} R w = 0$$  \hspace{1cm} (4.60)

where $\Omega$ denotes the domain of interest and $w$ are some "weights". Based on the choice of $w$ different weighted residual methods are obtained, such as the collocation, least squares and Galerkin methods [54].

Regardless of the particular method used to choose the weights $w$, two other parameters increase the efficiency of the solution in FEM. The first is related to the choice of piecewise continuous functions for the approximation $\tilde{u}(x)$. The second has to do with the fact that if the domain of interest is divided in a number of subdomains or "finite elements," then the solution obtained by the FEM becomes better for increasing number of elements. Therefore, instead of minimizing the residual defined in Equation 4.60 in the entire domain, the FE discretization and the use of piecewise continuous functions enable a similar efficient minimization to occur in each element, as shown in Equation 4.61.

$$I = \sum_{i=1}^{n} \int_{R_i} R w = 0$$  \hspace{1cm} (4.61)

where $n$ is the total number of FE.

**Stochastic finite elements background**

Randomness in materials and structures creates uncertainties in predictions of their overall mechanical behavior. In general, two sources of randomness are identified. The first
deals with the loads applied on a generalized medium and the second with its mechanical properties. In the case of random loads, the mathematical description of the medium's structure remains deterministic and, therefore, methods from random vibrations theory can be applied to determine the mechanical response [65]. However, the existence of randomly varying mechanical properties in space, such as the Young's modulus, has resulted in the formulation of a group of methods that are called stochastic finite elements (SFE). The interest in this area has grown in the last decades because it has been observed that even small uncertainties in the mechanical properties of materials affect their reliable use in applications [15].

The problem under consideration in SFE methods involves a general random medium which can be mathematically modeled using Equation 4.62, in accordance with the governing Equation 4.57.

\[ L(x, \theta)u(x, \theta) = F \]  

(4.62)

In Equation 4.62 \( L \) is a differential operator with randomly varying coefficients and \( u \) is a function that describes the random behavior of the medium. Furthermore, the parameter \( \theta \) is used to denote randomness.

For the model defined in Equation 4.62, three main types or SFE methods have been proposed. The first aims to compute the mean value, standard deviation and correlation function of the desired material properties, as for example in perturbation methods [49]. The second computes the probability of failure and includes the so-called reliability methods [40]. Finally the third aims at determining the entire probabilistic structure of the
response of a random medium to the externally applied loads, as for example in spectral SFE methods [29].

An alternative SFE method that can be used to compute the response of random media is the Monte Carlo simulation (MCS) technique [24, 58]. This technique is also used in the proposed MSFEM and, therefore, is described here.

MCS techniques are a powerful tool in probabilistic studies. The key advantage of MCS techniques compared to other SFE methods stems from the fact that the deterministic formulation of the problem remains unchanged when a Monte Carlo approach is followed. Therefore, instead of determining the random differential operator \( L \) which is needed to derive the random response \( u(x, \theta) \) in Equation 4.62, MCS techniques define the problem in terms of a set of random variables (RV) that represent, for example, the mechanical properties of a material. Next, in MCS the selected RV are quantified in terms of their statistical moments and probability density functions (PDFs). Given this information, values for the RV are numerically generated and for each set of values the deterministic problem is solved. Finally, the statistical processing of the ensemble of generated results for a large number of numerically simulated sets of values for the RV is used to extract information about the material properties. The accuracy of MCS in computing reliable estimates for the parameters of interest increases as the number of realizations increases. However, by increasing the number of MCS a significant increase in the computational time needed to perform the numerical simulations is also noticed and, therefore, several variance reduction techniques are applied to avoid this problem.
The use of MCS techniques in SFE methods for the determination of the mechanical properties of composite materials has been reported, for example, by Van Vinkenroy and de Wilde [108] and Graham and Baxter [35] among others. A review of the method for modeling of random heterogeneous materials is provided by Torquato [104].

**The proposed stochastic finite elements method**

Polymer nanocomposites are modeled in this dissertation as two-dimensional media. To determine their overall mechanical properties by the proposed MSFEM an elasticity problem is numerically solved using the finite element (FE) model presented next.

Figure 4.11 shows the procedure followed to formulate the FE model used in this dissertation for determining the mechanical properties of PNC. Examining Figure 4.11 it can be seen that the material region (MR) selected in section 4.2.1.1, and the grid of material points that quantify the local SWCNT volume fraction defined in section 4.2.1.2, are used to formulate the two-dimensional FE model presented in this figure. Thus, a value for the local SWCNT volume fraction is determined for each material point using the random field model described in section 4.2.1.3. This value is assumed constant in an area around each point. In this way, a continuum discretization is achieved if it is assumed that the area around each point corresponds to a FE. Additionally, the material microstructure in each FE is modeled in the proposed MSFEM by the two-phased medium presented in section 4.2.2.1, which consists of a hybrid matrix and spherical inclusions. The mechanical properties of these two phases are determined in the proposed FE model by using the Mori-Tanaka
Figure 4.11: The procedure followed in the proposed MSFEM to formulate a finite element model which is used to determine the mechanical properties of polymer nanocomposites. The random local SWCNT volume fraction is quantified in the grid of points defined in the selected material region (upper left). For each point an area is assigned where the volume fraction value is assumed constant. This area corresponds to a finite element in the continuum discretization (upper right). The microstructure in each finite element comprises the hybrid matrix and spherical inclusions (lower center).
homogenization method analyzed in section 4.2.2.2.

Furthermore, the developed FE model shown in Figure 4.11 is assumed to represent a "thin" plate in "plain stress" conditions. The term "thin" is used to denote that the thickness of the plate with respect to its other dimensions is significantly smaller. In the FE model shown in Figure 4.11, unit dimensions are assumed for the width W and height H of the thin plate, while the out-of-plane thickness is assumed to be equal to 0.01. Furthermore, only the in-plane static load P and the constraints shown in Figure 4.11 are applied on the boundary of the FE model and, therefore, plane stress conditions are valid. The thin plate model is a continuum idealization of the actual three-dimensional solid, and it reduces the computational time needed to determine the mechanical properties without compromising the accuracy of the numerical solution.

To determine the mechanical properties of PNC using the developed FE model, the elasticity problem of a thin plate subjected to the loads and boundary conditions shown in Figure 4.11 is solved. To this aim, three sets of equations are used, as in every solid mechanics problem. The first involves the equilibrium in the x and y axes shown in Equations 4.63 and 4.64, respectively.

\[
\frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} = 0 \quad (4.63)
\]

\[
\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \sigma_y}{\partial y} = 0 \quad (4.64)
\]

In Equations 4.63 and 4.64, it is assumed that no body forces are applied on the MR modeled, while \(\sigma, \tau\) denote the axial and shear stresses in the plate. The second set includes the constitutive equations which relate the stresses and strains in the plate, as shown in
Equation 4.65

\[ \{ \sigma \} = [T] \{ \varepsilon \} \]  \hspace{1cm} (4.65)

where \( \sigma \) is the stress and \( \varepsilon \) the strain tensor, defined in Equations 4.66 and 4.67, respectively.

\[ \{ \sigma \} = \{ \sigma_x, \sigma_y, \tau_{xy} \}^t \]  \hspace{1cm} (4.66)

\[ \{ \varepsilon \} = \{ \varepsilon_x, \varepsilon_y, \gamma_{xy} \}^t \]  \hspace{1cm} (4.67)

In Equations 4.66 and 4.67, \( \varepsilon \) and \( \gamma \) denote axial and shear strains where the exponent \( t \) means "transpose". Additionally, in Equation 4.65 \( T \) is the material's stiffness tensor.

Based on the analysis presented in section 4.2.2.1 of this chapter, both the hybrid matrix and the spherical agglomerates in each FE are isotropic materials. Consequently, the PNC modeled by the proposed MSFEM are also isotropic and, therefore, their stiffness tensor is given in Equation 4.68

\[ [T] = \frac{E}{1-\nu^2} \begin{bmatrix} 1 & \nu & 0 \\ \nu & 1 & 0 \\ 0 & 0 & \frac{1-\nu}{2} \end{bmatrix} \]  \hspace{1cm} (4.68)

where \( E \) is the Young's modulus and \( \nu \) the Poisson ratio. Finally, the third set includes the compatibility equations which describe the strain-displacement relationship, as shown in Equation 4.69
\[
\begin{pmatrix}
\varepsilon_x \\
\varepsilon_y \\
\gamma_{xy}
\end{pmatrix}
= \begin{pmatrix}
\frac{\partial u}{\partial x} \\
\frac{\partial v}{\partial y} \\
\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}
\end{pmatrix}
\]

(4.69)

where \(u, v\) are the displacements in the \(x\) and \(y\) axis, respectively.

In the FE model of the thin plate used in the proposed MSFEM for determining the mechanical properties of PNC, an approximate solution for the nodal displacements in each FE is assumed, following the procedure described for deterministic FE methods. Therefore, based on Equation 4.58, in each FE

\[
u(x) \approx \tilde{u} = [N] \{a\}
\]

(4.70)

where \(u = \{u, v\}^T\) denotes the displacement in the \(x\) and \(y\) axis, \([N]\) is the matrix of shape functions, defined in Equation 4.71

\[
[N] = [N_1(x, y) \ N_2(x, y) \ N_3(x, y) \ N_4(x, y)]
\]

(4.71)

and \(\{a\} = \{u_1, v_1, u_2, v_2, u_3, v_3\}^T\) are the values of the nodal displacements. Therefore,

\[
\begin{pmatrix}
u \\
v
\end{pmatrix}
= \begin{bmatrix}
N_1 & 0 & N_2 & 0 & N_3 & 0 & N_4 & 0 \\
0 & N_1 & 0 & N_2 & 0 & N_3 & 0 & N_4
\end{bmatrix}
\begin{pmatrix}
u_1 \\
v_1 \\
u_2 \\
v_2 \\
u_3 \\
v_3 \\
u_4 \\
v_4
\end{pmatrix}
\]

(4.72)
Given Equations 4.69 and 4.72, an expression for the strains in the FE is also obtained, as shown in Equation 4.73

$$\{\epsilon\} = [M] \{a\} \quad \text{(4.73)}$$

where

$$[M] = \begin{bmatrix} \partial N_1 & 0 & \partial N_2 & 0 & \partial N_3 & 0 & \partial N_4 & 0 \\ 0 & \partial N_1 & 0 & \partial N_2 & 0 & \partial N_3 & 0 & \partial N_4 \end{bmatrix} \quad \text{(4.74)}$$

Based on this formulation the stiffness matrix of each FE, \([K^{FE}]\) can be expressed as in Equation 4.75 [54].

$$[K^{FE}] = \int_{V_{FE}} [M]^T [T] [M] dV \quad \text{(4.75)}$$

After computing the element stiffness matrix for all FE, the global stiffness matrix \([K]\) is assembled and the nodal displacements \(\{a\}\) are determined by solving Equation 4.76

$$[K] \{a\} = [F] \quad \text{(4.76)}$$

where \([F]\) is the matrix that describes the loads. Knowledge of the nodal displacements allows the computations of strains and, therefore, estimates for the Young’s modulus and the Poisson ratio of the entire plate can be determined by assuming linear elastic behavior.

To extract reliable information about the mechanical properties of PNC using the proposed MSFEM, multiple realizations of the random field that describes that local SWCNT
volume fraction in polymers are generated. For each realization, the FE model is used to compute estimates for the mechanical properties of PNC by numerically solving the two-dimensional elasticity problem described in this section. Therefore, Equation 4.76 can be written as

\[
[K(\theta)] \{a(\theta)\} = [F]
\]

(4.77)

where \( \theta \) denotes that a realization of the random field is used for each FE solution. The ensemble of derived values for these properties is subsequently post-processed to compute the mean value and standard deviation of the FE estimates, which allows the determination of the mechanical properties of PNC in a statistical way.

The MSFEM developed in this chapter is used in three applications. Specifically, Chapter 5 describes the determination of the effective Young’s modulus and Poisson ratio of PNC. Chapter 6 presents a model for determining the Young’s modulus of PNC based on numerically generated nanoindentation data. Finally, Chapter 7 describes the application of the MSFEM in modeling of the elastic stability of PNC structures. In each application, various components of the MSFEM are modified to achieve the desired goals. Overall, the implementation of the developed method in applications pertinent to the determination of the mechanical behavior of PNC shows the unique contribution of this dissertation.
Chapter 5

Characterization of Mechanical Properties of PNC

The multiscale stochastic finite elements method (MSFEM) developed in Chapter 4 is used in Chapter 5 to determine the Young’s modulus (YM) and Poisson ratio (PR) of polymer nanocomposites (PNC). Specifically, two particular PNC are modeled in this chapter; they are referred to as “case 1” and case 2, for convenience. Case 1 includes an epoxy and case 2 a polyvinyl alcohol (PVA) polymer, both of which are reinforced with single-walled carbon nanotubes (SWCNT). The proposed MSFEM yields estimates for the YM and PR which are in good agreement with pertinent experimentally measured values reported in the literature.
5.1 Experimental information

Experimental information about the fabrication and post-treatment of the epoxy and PVA-matrix nanocomposites modeled in this chapter is presented in the articles by Zhu et al. [127] and Paiva et al. [79], respectively. The following sections analyze this experimental evidence to support choices made in the proposed MSFEM.

5.1.1 Case 1: Epoxy nanocomposite

Zhu et al. [127] fabricated, characterized and tested a nanocomposite that consisted of an epoxy matrix reinforced with SWCNT. The epoxy resin used was a diglycidyl ether of biphenol-A epoxy EPON 862 with a curing agent EPON W. The mixing of the nanotubes with the polymer system was achieved by sonication and high shear mixing (see section 3.2.1). Finally, the mixture was cured in an oven. This procedure was repeated for two SWCNT weight percentages equal to 1% and 4%, respectively.

The SWCNT used in case 1 were produced by the HiPCO method (see section 2.4.2). The diameter of the nanotubes was estimated at 1-1.4 nanometers, and their length from 100nm to micrometers. The SWCNT were functionalized before they were mixed with the polymer. Specifically, hydrochloric (HCL) acid was used to terminate the open ends of the nanotubes with carboxylic acid groups. The nanotube sidewalls were further functionalized using ethylcarboxyl groups to prevent the formation of excess cross-links among nanotubes. Figure 5.1 shows an SEM image of the functionalized SWCNT before mixing. As can be seen in this figure, a highly entangled network of SWCNT bundles constitutes
the reinforcement phase before mixing in the PNC reported by Zhu et al.

Figure 5.1: SEM image of the functionalized SWCNT before mixing used by Zhu et al. [127]. A highly entangled network of SWCNT bundles is observed in this image.

Zhu et al. also performed tensile tests on samples of the epoxy nanocomposite using a screw-driven machine according to pertinent standard experimental procedures. For each SWCNT weight percentage, five to ten samples were tested to determine the YM of the PNC and its standard deviation. The reported results are shown in Table 5.1.

Table 5.1: The experimentally measured Young’s Modulus of the nanocomposite reported by Zhu et al. [127].

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s Modulus (MPa)</th>
<th>Standard deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>2026</td>
<td>78</td>
</tr>
<tr>
<td>1% PNC</td>
<td>2650</td>
<td>125</td>
</tr>
<tr>
<td>4% PNC</td>
<td>3400</td>
<td>253</td>
</tr>
</tbody>
</table>

Based on the results presented in Table 5.1 it can be concluded that the values for the
YM of the PNC determined by tensile tests are higher compared to the one of the neat polymer. Hence, SWCNT enhance the mechanical properties of PNC. This observation is further supported by the dynamic mechanical analysis (DMA) results reported in [127]. Additionally, Zhu et al. observe that as the SWCNT content in the polymer increases, the viscosity of the resulting nanocomposite also increases and, therefore, the dispersion of nanotubes in polymers becomes more difficult; voids are also observed. Consequently, Zhu et al. suggest that there should be an upper limit in the amount of SWCNT mixed with polymers to avoid poor dispersion. Therefore, the effect of SWCNT agglomeration and concentration on the mechanical properties of PNC is quantified in the proposed MSFEM.

Figure 5.2: SEM image of the fracture surface of the polymer nanocomposite with 1% (weight) SWCNT [127]. The length scale in this image is on the order of $\mu m$; therefore the brighter spots correspond to SWCNT bundles or agglomerates, which seem to be randomly dispersed in the polymer.

Figure 5.2 shows an image of the fracture surface of the nanocomposite with 1% (weight) SWCNT. Examination of this image shows that the scale is in the order of $\mu m$ and, therefore, the observed brighter spots correspond to SWCNT bundles or agglomerates.
which have various diameters and are non-uniformly dispersed in the polymer matrix. In addition, Zhu et al. report that the observed SWCNT formations are broken and not pulled-out which means that the interfacial bonding between the polymer and the nanotubes is good. Therefore, the assumptions of non-uniform dispersion and perfect bonding made in the proposed MSFEM are supported by experimental characterization results.

5.1.2 Case 2: PVA nanocomposite

Paiva et al. [79] fabricated, characterized and tested a nanocomposite that consisted of a PVA matrix reinforced with SWCNT which were produced using the chemical vapor deposition method (see section 2.4.2) and functionalized with low molecular weight PVA. The dispersion of the carbon nanotubes in the polymer matrix was achieved by sonication and stirring procedures. Thin films of neat and reinforced PVA were fabricated for material characterization and testing purposes. Two SWCNT weight percentages equal to 2.5% and 5% were used.

Table 5.2 shows the results of the tensile tests conducted on the PVA-matrix nanocomposite fabricated by Paiva et al. The mean values and standard deviations of the YM values shown in Table 5.2 were computed using the data from a minimum of four tested samples.

The experimental results shown in Table 5.2 indicate the reinforcement role of SWCNT. Specifically, the measured YM values of the PNC are 40 % (2 % SWCNT) and 55 % (5% SWCNT) greater than the corresponding one for the neat PVA. Figure 5.3 shows an example of the fracture surface of one of the samples of the nanocomposite tested by Paiva
Table 5.2: The experimentally determined Young’s modulus of the nanocomposite fabricated by Paiva et al. [79].

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s Modulus (GPa)</th>
<th>Standard deviation (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PVA</td>
<td>4</td>
<td>0.1</td>
</tr>
<tr>
<td>2.5% PNC</td>
<td>5.6</td>
<td>0.4</td>
</tr>
<tr>
<td>5% PNC</td>
<td>6.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

et al. At the length scale of Figure 5.3, only some SWCNT aggregates and bundles are observed. Based on this observation, Paiva et al. claim good dispersion of nanotubes in the polymer matrix as a result of the functionalization and mixing procedures used. However, the same authors provide no additional images or information about the PNC structure at higher magnifications and, therefore, their assumption of homogeneous nanotube dispersion is not justified.

Figure 5.3: SEM micrograph of the fracture surface of the polymer nanocomposite fabricated and tested by Paiva et al. [79]. Some SWCNT aggregates and bundles (brighter areas in the image) are observed on a generally smooth surface.
For the purposes of the MSFEM method proposed in this dissertation, the experiments conducted by Paiva et al. serve as a basis for comparison of the numerically computed values of the Young's modulus and Poisson ratio of PNC. As it shown in this chapter, for SWCNT weight percentages on the order of 2.5-5 %, their agglomeration is an important parameter that affects the dispersion of SWCNT in polymers and consequently their mechanical properties.

5.2 Modeling results

The MSFEM proposed in this dissertation is used to determine YM and PR values of the nanocomposite materials presented in section 5.1. Since no images are available of the exact structure before testing of the PNC modeled in this chapter, a general material region (MR) similar to the one presented in Figure 4.4 is assumed. In this MR, a number of points are specified to quantify the spatial variation of the local SWCNT volume fraction in PNC. To investigate the effect of the number of chosen material points on the computed estimates of the YM and PR, various mesh sizes are used and include 1, 4, 9, 25, 36, 49, 64, 81 and 100 grid points.

At each point of the selected MR, the local SWCNT volume fraction is represented by a random variable, as explained in the model developed in section 4.2.1.2. For the purposes of the Monte Carlo finite element scheme used in the proposed MSFEM, a collection of 500 realizations of vectors that contain values for these random variables are numerically generated in MATLAB for each SWCNT weight percentage (wt).
To compute the local volume fraction percentages (vf), Equation 4.56 is used, in which the polymer and SWCNT density values must be specified. To this aim, in the proposed MSFEM the density values for the epoxy resin and PVA matrices were found in the literature and are equal to 1.125 and 1.25 $g/cm^3$, respectively. Regarding the SWCNT density, Equation 2.7 is used, in which the SWCNT diameter is assumed to be equal to 1.8 $nm$, as computed by the model suggested by Odegard et al. [73]. Therefore, all SWCNT in the proposed MSFEM have the same diameter and, consequently, the same density which is found to be equal to 1.371 $g/cm^3$.

Furthermore, based on the density values of the polymers and the SWCNT, the SWCNT vf in case 1 are equal to 0.822% and 3.306%, and the corresponding ones in case 2 are equal to 2.28% and 4.58%. In each case, the two vf involved are referred to as VF1 and VF2. It is further noted that the random values in each numerically generated vector are scaled accordingly, so that their mean value is always equal to either VF1 or VF2. Figure 5.4, shows examples of such vectors which contain values that have the three probability density functions defined in Equations 4.27, 4.28 and 4.29, mean values equal to VF1 and VF2 of case 1 and various standard deviations. The effect of the standard deviation on the numerically computed values of the mechanical properties of PNC is also discussed in this section.

Based on the methodology presented in section 4.2.2.3 of this dissertation, a Finite Elements (FE) problem is formulated. Figure 4.11 provides an illustration of the geometrical domain that represents thin plates of the nanocomposite materials modeled in this chapter.
Figure 5.4: Examples of vectors of random values that have uniform, beta and log-normal distributions. The three plots on the left correspond to SWCNT volume fraction equal to 0.822% (VF1) and the ones on the right to 3.306% (VF2). In all plots, the horizontal axis shows the values for the random local SWCNT volume fraction (in percentage), and the vertical axis the number of times these values appear in samples of 100 values.
The FE discretization coincides with the random field discretization imposed by the grid of material points in which the values of the local SWCNT volume fractions are quantified. Therefore, the number of FE is equal to the number of grid points in the MR.

In each FE, PNC are modeled as two-phased media implementing the analysis presented in section 4.2.2.1 of this dissertation. To determine the local mechanical properties of the nanocomposite at each FE, the Mori-Tanaka (MT) method is used. To this aim, based on the value of the SWCNT volume fraction in each FE, the proposed MSFEM determines the dispersion and agglomeration indices defined in Equations 4.37 and 4.35, respectively. Specifically, these indices are determined by using the experimental evidence available in the literature. Therefore, based on the definition of the dispersion index $\zeta$, the closer it is to 1 for $\zeta > \xi$ the more heterogeneous the structure is. Additionally, it is true that as $\xi$ approaches 0, the PNC becomes more heterogeneous. Moreover, it has been reported by Zhu et al. [127], that for SWCNT volume fractions greater than 4%, the viscosity of the PNC is high and, therefore, the dispersion of nanotubes in the polymer presents non-uniform characteristics. Based on these remarks, the proposed MSFEM determines adaptively the values for the dispersion and agglomeration indices by using the value for the local SWCNT volume fraction in each FE and by choosing the degree of heterogeneity. Hence, for a given value of the local SWCNT volume fraction in each FE, the dispersion index quantifies the amount of SWCNT in the polymer and the inclusions, while the agglomeration index denotes the degree of heterogeneity.

Based on the values of $\zeta$ and $\xi$, the MT method is used first to compute the elastic
parameters of the hybrid matrix, shown in Figure 4.7. To this aim, both the epoxy and PVA matrices are assumed isotropic to take advantage of the Eshelby result presented in section 4.2.2.2. The YM of the epoxy and PVA matrices are taken from the experimental results shown in Tables 5.1 and 5.2 and their PR are assumed equal to 0.3 [93] and 0.48, respectively. Furthermore, all SWCNT in the proposed MSFEM are assumed to be straight, transversely isotropic (their elastic parameters are shown in table 4.1), perfectly randomly oriented and perfectly bonded to polymers. In this case, the hybrid matrix schematically shown in Figure 4.7 is also isotropic and its YM and PR are determined by using the MT method, in which the aspect ratio of the SWCNT is specified. Based on experimental evidence and to support the assumption of straight SWCNT, their aspect ratios in the proposed MSFEM are all equal to 200. Taking into consideration that the diameter of the SWCNT is assumed equal to 1.8 nm, using the model by Odegard et al. [73], this choice of SWCNT aspect ratio corresponds to a mean length of SWCNT in polymers equal to 111.11 nm.

Figure 5.5 shows the values for the YM and PR of the hybrid matrix computed for a range of CNT aspect ratios by assuming homogeneous dispersion of SWCNT in the matrix and SWCNT volume fractions equal to VF1 and VF2. By examining Figure 5.5, one can conclude that the SWCNT aspect ratio affects the computed values for the YM and PR of the PNC in both cases. However, this effect becomes less important for aspect ratio values greater than 200, as shown in Figure 5.5.

Figure 5.6 shows the effect of SWCNT volume fraction on the YM and PR values of the hybrid matrix computed by the MT method. The SWCNT are again assumed to be
Figure 5.5: The Young's modulus and Poisson ratio values of the hybrid matrix computed by the Mori-Tanaka method. The SWCNT volume fractions are equal to VF1 and VF2, respectively. The figure shows that the choice of SWCNT aspect ratio affects the computed values. However, for aspect ratio values greater than 200, the computed values do not change significantly.
straight, homogeneously dispersed, perfectly randomly oriented and perfectly bonded to the polymer matrices. In addition, the SWCNT aspect ratio is equal to 200. As can be seen in Figure 5.6, the computed YM and PR values increase significantly as the SWCNT volume fraction increases.

Moreover, Figure 5.7 shows the effect of the dispersion and agglomeration indices on the local YM and PR values of the PNC in each FE computed by the MT method. On the one hand, it can be seen that the closer to 1 the dispersion index is, the more heterogeneous are the PNC. Hence, as $\zeta$ decreases, the local YM increases and the local PR decreases. On the other hand, the closer to 0 the agglomeration index is, the more heterogeneous are the PNC. Hence, as $\xi$ decreases, the local YM decreases and the local PR increases.

The MT method is subsequently used to compute the local YM and PR values in all FE, by assuming that the PNC structure is the one presented in section 4.2.2.1. In this way, material property fields such as the ones presented in Figure 5.8 are generated, and they are subsequently used to solve the static FE problem of a thin plate subject to axial loading. These material property fields represent the spatial variation of the local YM and PR values in PNC.

Since the material properties in each FE are known and represented by random fields similar to the ones shown in Figure 5.8, for each realization the FE problem described in section 4.2.2.3 of this dissertation is solved. To compute the YM value for the PNC for each realization, the strains in the vertical direction in all FE are computed and averaged. Hence, using the assumption of linear elastic behavior, the YM value is computed by dividing
Figure 5.6: The Young's modulus and Poisson ratio values of the hybrid matrix as computed by the Mori-Tanaka method for a range of SWCNT volume fraction values ranging from 0 to 25 (%). The SWCNT aspect ratio is assumed equal to 200.
Figure 5.7: Local values of the Young’s modulus (YM) and Poisson ratio (PR) of the PNC computed by the Mori-Tanaka method for SWCNT volume fractions equal to VF1 and VF2. The decrease of the agglomeration index $\xi$ causes a decrease of the local YM and an increase of the local PR. On the contrary, a decrease of the dispersion index $\zeta$ increases the local YM and decreases the local PR.
Figure 5.8: Sample realizations of the Young's modulus and Poisson ratio random fields computed by using the Mori-Tanaka method in the agglomerated two-phase model of the PNC in each FE. The material properties of case 1 and SWCNT equal to VF1 are used. It can be seen that the choice of probability distribution affects the fluctuations observed in these realizations.
the applied stress by the mean strain. This procedure is repeated for all 500 realizations of the material random fields; the mean values and standard deviations of the ensemble of results are determined. Similarly, to compute the PR value for each realization, the vertical and horizontal strains in all FE are computed and averaged. The PR value is then computed by dividing the mean vertical over the mean horizontal strain. The ensemble of PR values collected for all 500 realizations is used to determine their mean value and standard deviation.

The procedure previously described to compute the YM and PR values of PNC is repeated for each FE mesh size and each SWCNT volume fraction value. It should be noted here that the YM and PR values that are computed in the case of one FE represent the MT values. As will be shown in the following figures, the direct application of the MT method to compute estimates of the mechanical properties of PNC is not appropriate for PNC, since this method cannot incorporate all information about the local material properties and structure. This problem is rectified by the proposed MSFEM which uses the MT method as part of a model that incorporates this local information and determines the overall mechanical properties of PNC.

Figure 5.9 shows the mean values of the YM computed for the nanocomposite material of case 1, for SWCNT volume fraction equal to VFI and four different values of the standard deviation for each probability distribution. As can be seen in this figure, the MT value is always higher than all values computed using larger FE mesh sizes. In addition, Figure 5.9 shows that, for all three probability distributions, the increase of the standard deviation
of the random volume fraction vectors shown in Figure 5.4 decreases the computed YM values. In addition, Figure 5.10 shows similar results for a SWCNT volume fraction equal to VF2. Again, the increase of the standard deviation decreases the estimates of the YM computed by the proposed MSFEM.

Moreover, Figures 5.11 and 5.12 present the corresponding results of the YM for the nanocomposite material in case 2 and for both SWCNT volume fractions. In these figures, it can be seen again that the standard deviation affects the YM values. However, although in Figures 5.11 and 5.12 the YM values decrease as the standard deviation increases, the MT value for SWCNT volume fraction equal to VF2 is not always higher compared to the YM values for larger mesh sizes.

Collectively, Figures 5.9, 5.10, 5.11 and 5.11 show that the increase of the standard deviation causes a decrease of the YM values in all cases investigated in this section. Hence, by appropriately selecting the standard deviation of the random samples of local SWCNT volume fractions, a closer agreement with experimental results can be achieved as shown in subsequent figures in this section.

Furthermore, it should be noted that, although for SWCNT volume fractions equal or less than 4% the MT values constitute an upper bound for the values computed by the MSFEM, this is not true in the case of higher SWCNT volume fractions, as, for example, shown in Figure 5.12. Therefore, it is shown that the proposed MSFEM is capable of determining the mechanical properties of PNC by incorporating crucial information about their local structural features.
Figure 5.9: The mean values plus and minus one standard deviation of the Young's modulus computed by the proposed MSFEM for the material of case 1 and SWCNT volume fraction equal to VF1. The choice of standard deviation for the random samples presented in Figure 5.4 affects the computed results.
Figure 5.10: The mean values plus and minus one standard deviation of the Young’s modulus computed by the proposed MSFEM for the material of case 1 and SWCNT volume fraction equal to VF2. The choice of standard deviation for the random samples presented in Figure 5.4 affects the computed results.
Figure 5.11: The mean values plus and minus one standard deviation of the Young's modulus computed by the proposed MSFEM for the material of case 2 and SWCNT volume fraction equal to VF1. The choice of standard deviation for the random samples presented in Figure 5.4 affects the computed results.
Figure 5.12: The mean values plus and minus one standard deviation of the Young's modulus computed by the proposed MSFEM for the material of case 2 and SWCNT volume fraction equal to VF2. The choice of standard deviation for the random samples presented in Figure 5.4 affects the computed results.
It should also be noted here that the variations observed in the values for the PR of the PNC by increasing the FE mesh size and/or by increasing the standard deviation are small and thus, all values are very close to the ones computed by the MT method. This is why figures similar to Figures 5.9, 5.10, 5.11 and 5.12 are not presented here. However, figures that show the PR values for the PNC modeled in this chapter are presented later for completeness.

Based on the experimental results presented in Tables 5.1 and 5.2 and the modeling results shown in Figures 5.9, 5.10, 5.11 and 5.12, the values for the standard deviations are chosen in each case to match better the experimental results. The choice of the standard deviation and the other components of the proposed MSFEM aim to model the variations in the non-uniform dispersion of SWCNT in polymers which depend on the effectiveness of the various fabrication methods. Hence, the proposed MSFEM models the variations in the spatial distribution and dispersion of SWCNT in polymers and, as it is shown next, it succeeds in computing values for the mechanical properties of PNC which agree with pertinent experimental results.

Figures 5.13 and 5.14 show the numerically computed mean values plus and minus one standard deviation of the effective YM of the nanocomposite in case 1. These figures also include the experimental results obtained by Zhu et al. [127]. All YM values in Figures 5.13 and 5.14 are normalized by the mean experimental values in [127]. In Figure 5.13 the standard deviations used are equal to 0.047, 0.074 and 0.0075 for the uniform, beta and log-normal distributions, respectively. The corresponding values for Figure 5.14 are
0.0167, 0.023 and 0.03, respectively.

Figure 5.13 shows that the mean values of the estimates for the effective YM computed by the proposed MSFEM are always within the bounds defined by the mean experimental value plus and minus one standard deviation. However, since the MT value (i.e., the value for one FE) is lower than the experimental mean value, all numerically computed values for larger mesh sizes are also lower. Nevertheless, the difference is less than 4% for all probability distributions. It should also be noted that for a SWCNT volume fraction equal to VF1, the dispersion of nanotubes in the polymer is expected to be close to uniform, and therefore, the chosen standard deviations are relatively small to comply with this fact.

In Figure 5.14 it can be seen that the mean values of the estimates of the YM computed numerically are always less than 1% different from the experimental ones. This comparison shows the effectiveness of the proposed MSFEM to compute reliable estimates of the mechanical properties of PNC. Moreover, it is noted that the MT value in this case is above the experimental bounds, supporting the fact that the direct application of this method in the case of PNC is not appropriate.

Regarding the effect of the number of FE on the computed estimates of the YM in case 1, it can be seen in Figure 5.15 that by increasing the FE mesh size the coefficient of variation (COV), defined as the mean value over the standard deviation, of the numerical results decreases rapidly as the number of FE increases. The decrease of the COV indicates the optimum number of FE that should be used to compute numerically the effective YM of PNC.
Figure 5.13: Mean values plus and minus one standard deviation of the effective Young's modulus (YM) of the PNC determined by the proposed MSFEM and compared with the experimental results reported by Zhu et al. [127]. All values are normalized with the mean experimental value of the YM measured by tensile tests of PNC with SWCNT volume fraction equal to VF1. Results are given for the three probability distribution functions used in the MSFEM.
Figure 5.14: Mean values plus and minus one standard deviation of the effective Young’s modulus (YM) of the PNC determined by the proposed MSFEM and compared with the experimental results reported by Zhu et al. [127]. All values are normalized with the mean experimental value of the YM measured by tensile tests for SWCNT volume fraction equal to VF2. Results are given for the three probability distribution functions used in the MSFEM.
Figure 5.15: Coefficient of variation of the normalized Young's modulus (YM) values computed by the proposed MSFEM and shown in Figure 5.13 and 5.14 versus the number of finite elements. The two curves correspond to the YM values computed for both SWCNT volume fractions. Results are given for the three probability distribution functions used in the MSFEM.
For the nanocomposite material in case 2, Figure 5.16 and Figure 5.17 show the mean values of the YM computed by the MSFEM for both SWCNT volume fractions. Hence, for VF1 the standard deviations used are equal to 0.013, 0.016 and 0.02 for the uniform, beta and log-normal distributions, respectively. The corresponding values for VF2 are 0.026, 0.04 and 0.05.

Figure 5.16 shows the YM values computed by the MSFEM for SWCNT volume fraction equal to VF1. These values are compared to the experimental ones measured by Paiva et al., which are reported in Table 5.2. All values in this figure have been normalized with the mean experimental value for VF1 equal to 5.6 GPa. As can be seen in Figure 5.16 the YM values for all three probability distributions are always in the bounds determined by the experimental mean value plus and minus one standard deviation. The numerical values are, further, found to be less than 1% different from the mean experimental value.

However, for a SWCNT volume fraction equal to VF2 the YM values computed by the uniform distribution and shown in Figure 5.17 approach only the upper experimental bound, indicating that this particular distribution is not appropriate for large concentrations of nanotubes. However, the results obtained using the beta and log-normal distributions are again less than 1% different from the mean experimental value. The MT estimate in this case is out of the experimental bounds.

Moreover, the effect of the number of FE on the COV of the YM is shown in Figure 5.18. As seen in this figure, the increase of the FE mesh size causes a decrease of the COV.

Regarding the values for the effective PR of the PNC computed by the MSFEM, Figure
Figure 5.16: Mean values plus and minus one standard deviation of the effective Young's modulus (YM) of the PNC determined by the proposed MSFEM and compared with the experimental results reported by Paiva et al. [79]. All values are normalized with the mean experimental value of the YM measured by tensile tests for SWCNT volume fraction equal to VF1. Results are given for the three probability distribution functions used in the MSFEM.
Figure 5.17: Mean values plus and minus one standard deviation of the effective Young's modulus (YM) of the PNC determined by the proposed MSFEM and compared with the experimental results reported by Paiva et al. [79]. All values are normalized with the mean experimental value of the YM measured by tensile tests for SWCNT volume fraction equal to VF2. Results are given for the three probability distribution functions used in the MSFEM.
Figure 5.18: Coefficient of variation of the normalized Young's modulus (YM) values computed by the proposed MSFEM and shown in Figure 5.16 and 5.17 versus the number of finite elements. The two curves correspond to the YM values computed for both SWCNT volume fractions. Results are given for the three probability distribution functions used in the MSFEM.
5.19 presents the pertinent results. No experimental data are available for comparison in the case of the PR of PNC. Therefore, the values computed by the MSFEM are compared to the one obtained by the MT method. Figure 5.19 shows that the effect of the spatial randomness in the structure of PNC on their effective PR values is negligible. Consequently, it is concluded that the estimates for the PR of PNC computed by using the MT method are reliable.

Figure 5.19: The estimates for the effective Poisson ratio (PR) of the PNC in cases 1 and 2 and both SWCNT volume fractions. The figure shows that the estimates computed by the proposed method agree with the values obtained by the direct application of the MT homogenization method. Consequently, it is concluded that the effect of the spatial randomness in PNC on the values of their PR is negligible.

In summary, Chapter 5 shows the success of the proposed MSFEM in determining
accurate and reliable estimates of the Young’s modulus and Poisson ratio of PNC. Hence, it has been shown in this chapter that the incorporation of nano- and microscale information pertinent to the spatial distribution of SWCNT in polymers in the proposed multiscale numerical method yields results that agree with available experimental data.
Chapter 6

Modeling of Nanoindentation Data

Chapter 6 presents an additional application of the proposed MSFEM in the area of characterization and modeling of the mechanical behavior of polymer nanocomposites. Specifically, the method presented in chapter 4 is modified in this chapter to numerically generate data which are compatible with experimental nanoindentation (NI) measurements. Subsequently, the method is used in conjunction with the spectral representation method and with a Monte Carlo finite elements scheme to determine accurately and reliably the overall Young’s modulus (YM) of PNC. The numerical results show that the effects of the spatial variation in the local mechanical properties on the overall material behavior are significant and, therefore, they should be incorporated in modeling. The numerical results presented in this chapter agree with pertinent experimental tensile test findings analyzed in Chapter 5.
6.1 The nanoindentation method

Section 3.2.4.3 of this dissertation presents the experimental procedure followed to characterize the mechanical properties of materials using the NI method. Specifically, Figure 3.9 shows the loading-unloading path used to determine local estimates of the YM and hardness of materials. Each such estimate is computed based on data collected by performing a number of indentations on the material sample as shown in Figure 6.1. Usually, the NI procedure illustrated in Figure 6.1 is repeated for various indentation depths to avoid issues related to differences between the surface and the bulk material. Furthermore, the NI procedure is repeated for all available samples of the material. The estimates of the effective YM are subsequently computed by averaging all available data for each penetration depth.

Figure 6.1: Image showing multiple indentations performed experimentally on the surface of a sample of a polymer nanocomposite (courtesy of Professor D.C. Lagoudas, Texas A&M University).
An example of experimental NI results is shown in Figure 6.2. The results in Figure 6.2 are presented in the form of curves which show the variation of the estimates of the effective YM of a PNC with increasing indentation depth. Therefore, for each indentation depth, a number of local YM values is computed by using NI measurements similar to the ones shown in Figure 6.1. These values are then averaged to compute the estimates of the effective YM of the PNC. Although general trends regarding the effective YM of PNC with increasing SWCNT weight percentage can be observed by simply averaging local YM values, the proposed estimates in Figure 6.2 present significant variations. This is most likely caused by the limited number of experimental findings and the consideration of just the mean value of a statistically small data set.

Consequently, the effective YM estimates determined by the NI method are often found to be significantly different compared to corresponding ones measured, for example, by conducting tensile tests [18]. Therefore, the uncertainty related to the use of the NI method in characterization of the mechanical properties of materials is significant. To rectify this problem, the proposed MSFEM is appropriately modified to numerically generate NI data which are subsequently modeled to obtain estimates of the effective YM of PNC.

Therefore, the application of the proposed MSFEM presented in Chapter 6 describes a modeling procedure of NI data. This chapter shows that the proposed modeling procedure provides two kinds of useful information related to PNC. First, the use of the numerically generated NI data as input to the Monte Carlo (MC) finite element (FE) part of the proposed method yields reliable estimates of the effective YM of PNC. Consequently, the proposed
Figure 6.2: Example of experimental NI results reported in [18]. The figure shows the effect of various SWCNT volume fractions on the estimates of the YM of PNC. The YM estimates for each indentation depth are computed by averaging local YM values obtained by following a procedure similar to the one presented in Figure 6.1. Significant variations of the YM estimates are observed with increasing indentation depth caused by averaging the limited available experimental data.

The procedure reduces the uncertainty caused by averaging a limited number of experimentally obtained NI data, as shown in section 6.3. Second, the numerical generation of the NI data is performed by using the micromechanics homogenization model described in Chapter 4. This practically means that actual experimental NI data that provide values for the local YM of PNC can be used to calibrate the choice of certain parameters in the proposed MS-FEM. Hence, the proposed method, after validation, can be a link between the material’s local mechanical behavior and its nano-/micro structure. Chapter 8 provides some more information about possible extensions of the proposed method in modeling of the mechanical behavior of PNC.
6.2 Generation and modeling of nanoindentation data

The proposed MSFEM is used in Chapter 6 to rectify the problem of determining unreliable and inaccurate estimates of the YM of PNC by using data obtained in NI tests. Specifically, actual experimentally obtained NI data are viewed in the proposed modeling procedure as measurements of the local YM of PNC. Consequently, the proposed model treats the non-uniform/non-homogeneous dispersion of SWCNT in polymers as source of uncertainty in the reported NI data. Consequently, the method developed in Chapter 4 is used in this section to model the effects of the spatial randomness in local mechanical properties of PNC on their overall YM.

Figure 6.1 shows that to determine the YM of PNC using NI tests, multiple indentations are performed in a grid of selected material points for each indentation depth. Therefore, two-dimensional arrays of YM values are obtained that correspond to a grid of selected material points which coincide with the indentation locations. These YM values are subsequently averaged to compute estimates of the effective YM of PNC. It is interesting to note here that most experimental nanoindentation procedures reported in the literature show only the mean value of this kind of statistical analysis of experimental NI data while there is no reference to their standard deviation. A possible explanation could be the fact that the standard deviation computed based on experimental measurements is significant and, therefore, it is omitted to avoid reliability issues. However, the proposed MSFEM succeeds in providing reliable estimates of the effective YM of PNC. The reliability of the computed estimates is shown by the use of a specific statistical index as described in section 6.3.
The proposed model generates numerically NI data following the procedure schematically shown in Figure 6.3. Hence, the spatial variations in the local mechanical properties of PNC are created numerically by using the random field model developed in section 4.2.1.3 in combination with the two-phased micromechanics model shown in Figure 4.7.

![Diagram](image)

**Random Field Model**
- Model local CNT volume fraction

**Micromechanics Homogenization Model**
- Compute local Young's modulus values

**Spectral Representation Method**
- Generate samples of NI data

Figure 6.3: The procedure followed to generate numerically data which correspond to nanoindentation tests. This procedure is a modification of the random field model presented in Chapter 4.

Specifically, the procedure shown in Figure 6.3 is used to generate arrays of values that
represent discretizations of two-dimensional random fields of the YM in PNC. Hence, a
grid of material points similar to the one shown in Figure 4.4 is considered. This grid co-
cides with the locations where indentations are performed in actual NI tests. In addition,
the grid is chosen, without loss of generality, to be square. Furthermore, the total number
of points in it is always an odd number to take advantage of the Fast Fourier Transform
(FFT) version of the spectral representation method (SRM) used in the proposed model to
generate a statistically significant population of NI data.

Based on the random field model analyzed in section 4.2.1.3, a random variable (RV)
which quantifies the local SWCNT volume fraction is assigned to each material point.
Hence, a random vector of local SWCNT values is created, the values of which are as-
sumed to have a log-normal probability density function. This choice is based on the results
presented in Chapter 5, which show that the log-normal distribution succeeds in providing
YM estimates that agree with corresponding experimental results for all considered cases.
Next, a sample realization of the random vector of local SWCNT volume fractions is gen-
erated in MATLAB. It is noted here that, for the results presented in section 6.3, the mean
value of the random vector used for NI data generation is set equal to either VF1 or VF2
of the PNC in cases 1 and 2 which are presented in sections 5.1.1 and 5.1.2, respectively.
Moreover, the standard deviation of the random vector is set equal to the value that leads
to best agreement of the modeling and experimental results in Chapter 5. Therefore, the
standard deviation values for the log-normal distributions are equal to 0.005 and 0.03 for
VF1 and VF2 in case 1 and 0.02 and 0.05 for the corresponding volume fractions in case
2. This choice of standard deviation intends to show that even if the mean value of the YM estimates of a nanocomposite computed based on NI data is close to experimental tensile tests results, the use of small number of local YM values leads to significant variations that must be taken into account. Hence, the proposed method manages to incorporate the spatial randomness in the local YM values into a numerical scheme which computes reliable estimates for the effective YM of PNC.

After a random vector for each volume fraction value is generated, the finite element (FE) method presented in section 4.2.2.3 is used to discretize the material domain. In each FE the material structure is assumed to be the one shown in Figure 4.7. Hence, by applying the Mori-Tanaka homogenization procedure described in section 4.2.2.2, a two-dimensional array of values for the local YM of the PNC is obtained for each SWCNT volume fraction. This array represents the experimental NI data. Figure 6.4 shows examples of the generated arrays of YM values for each SWCNT volume fraction in the PNC of cases 1 and 2. For each of the YM arrays in Figure 6.4, the SRM is used to compute its mean value, standard deviation and power spectral density as is also shown in Figure 6.4. The SRM is further used to generate 500 realizations of each array of local YM values. Subsequently, each realization of each array is used in the Monte Carlo FE method described in section 4.2.2.3 to solve the static problem of a thin plate subject to axial loading. Consequently, an ensemble of estimates of the effective YM of the nanocomposite is obtained. The statistical analysis of the ensemble of numerically generated values is presented in section 6.3.
Figure 6.4: Examples of numerically generated nanoindentation data and their mean value, standard deviation and power spectrum computed by the spectral representation method. The results correspond to a square array which includes 121 local YM values.
6.3 Modeling results

In this section, numerically generated NI results are used to compute estimates of the effective YM of the PNC presented in sections 5.1.1 and 5.1.2 of this dissertation. The derived results are compared with the experimentally determined values shown in tables 5.1 and 5.2.

Following the procedure presented in Figure 6.3, NI data similar to the ones shown in Figure 6.4 are numerically generated. These data represent local YM values which can be used in the Monte Carlo FE method developed in section 4.2.2.3 to compute the effective YM of PNC. The array sizes used in section 6.3 are equal to 3x3, 5x5, 7x7, 9x9, 11x11, 13x13 and 15x15, respectively. An investigation of the optimum number of indentations needed to extract reliable estimates of the YM of PNC is performed by varying the array size. Furthermore, by varying the array size it is possible to observe its effect on the standard deviation of the YM estimates computed by the proposed model. It should be also noted that the effect of the number of realizations used in the Monte Carlo part of the proposed method on the derived results has also been investigated; it was concluded that 500 realizations are sufficient to yield small standard deviations for the YM estimates, as shown in the figures of this section.

Each of the subsequent figures shows the results derived by using the proposed procedure in modeling of NI data. Specifically, each figure comprises two plots. The one on the top shows normalized estimates for the effective YM of the PNC in cases 1 and 2. All YM estimates in this plot are normalized by the corresponding mean values determined by ten-
sile tests and presented in tables 5.1 and 5.2. Furthermore, each plot includes seven curves. The curves “SFEM Mean”, “SFEM Up” and “SFEM Low” show the mean values plus and minus one standard deviation of the YM estimates computed by the proposed model. The curves “Experimental”, “Exp Up” and “Exp Low” show the pertinent YM mean values plus and minus one standard deviation determined by the tensile tests. The seventh curve shows the YM estimates computed by averaging the numerically generated NI data. Moreover, the plot on the bottom of each figure shows the COV of the YM estimates computed by using the NI data and the corresponding COV of the ones computed by the proposed method. As shown in this section, in all plots the COV for the values that correspond to the proposed method is very close to zero which shows that the mean values derived based on the statistical analysis of the ensemble of the MC results are reliable estimates of the YM of PNC.

Figure 6.5 shows the derived results for the nanocomposite of case 1 and SWCNT volume fraction equal to VF1. As this figure shows, the YM values computed by the proposed method are lower with respect to the ones computed by the NI data for every FE mesh size. This is a first indication of the success of the proposed method taking into account the discrepancies reported in the literature between the YM values computed by NI data and the corresponding ones obtained by tensile tests. Furthermore, it can be observed in Figure 6.5 that the COV which corresponds to the NI data is almost equal to 15%, whereas the COV of the YM values computed by the proposed model is very close to zero. This remark shows that even if the YM estimates computed by averaging NI data are close
to other experimental results, their COV is such that it makes these values statistically unreliable. In contrast, the proposed method by means of the ensemble statistics of the population of values generated by the Monte Carlo FE method succeeds in reducing the standard deviation of the proposed estimates. In fact, the standard deviation of the estimates computed by the proposed method decreases with increasing FE mesh size. This is true for all figures presented in this section and has been also observed in the results presented in Chapter 5. An additional interesting remark can be made by observing both plots in Figure 6.5. Specifically, it can be seen that there is a correlation between the values of the normalized YM and their corresponding COV values for each FE mesh size. Hence, it can be concluded that the larger the COV of the YM values computed using NI data is, the lower are the corresponding values computed by the proposed method. Therefore, the use of the COV to evaluate the reliability of the suggested estimates for the effective YM of PNC shows that the averaging of NI data leads to significant statistical variations and, therefore, is unreliable.

Figure 6.6 shows the results which correspond to the nanocomposite of case 1 for SWCNT volume fraction equal to VF2. This figure shows that the YM values computed by averaging NI data are again always higher than the ones computed by the proposed method. In addition the COV of the values obtained by using the NI data is more than 18% for a FE mesh size equal to 81; the COV of the values based on the proposed method is almost equal to zero. Moreover, it is again obvious in this figure that as the COV of the YM values computed by NI data increases, the corresponding values computed by the proposed
Figure 6.5: Above: YM values for the nanocomposite in case 1 and SWCNT volume fraction equal to VF1. Below: Coefficient of variation of the YM values computed by averaging NI data and by using the proposed method.
Figure 6.6: Above: YM values for the nanocomposite in case 1 and SWCNT volume fraction equal to VF2. Below: Coefficient of variation of the YM values computed by averaging NI data and by using the proposed method.
method decrease.

Similar observations made for Figures 6.5 and 6.6 can be made for Figures 6.7 and 6.8. Specifically, Figures 6.7 and 6.8 show the results for the nanocomposite in case 2 and SWCNT volume fractions equal to VF1 and VF2, respectively. The YM estimates computed based on the proposed MSFEM are again always lower in these figures compared to the corresponding ones computed by averaging NI data; they are further found to be dependent on the COV of the NI data values. Hence, in Figure 6.8 the COV for 121 elements is almost equal to 30% and the normalized YM value computed by the proposed method is about 4% lower than the corresponding NI data value. Consequently, the application of the proposed MSFEM in modeling of NI data shows that in cases that the experimental data present significant statistical variations, then the expected estimates for the effective YM are much lower than the ones obtained by simply averaging. This conclusion must be taken into account in interpreting and handling of actual NI data.

In conclusion, the proposed MSFEM has been successfully modified in Chapter 6 to interpret and model NI data. Hence, indentation measurements are viewed by the proposed method as indicators of the spatial randomness in the local material properties caused by the non-uniform dispersion of SWCNT in polymers. Consequently, by incorporating the effect of the statistical variations in the structural reinforcement of PNC at a local level in modeling, the proposed method succeeds in providing reliable estimates of the effective YM of PNC based on NI data. Specifically, it is found that the suggested estimates for YM are always lower than the ones computed by direct averaging of NI data. In addition,
Case 2 - VF1

Case 2-VF1

Figure 6.7: Above: YM values for the nanocomposite in case 2 and SWCNT volume fraction equal to VF1. Below: Coefficient of variation of the YM values computed by averaging NI data and by using the proposed method.
Figure 6.8: Above: YM values for the nanocomposite in case 2 and SWCNT volume fraction equal to VF2. Below: Coefficient of variation of the YM values computed by averaging NI data and by using the proposed method.
the suggested YM estimates have very small standard deviations which further decrease as the number of FE increases. Of additional interest is the fact that the YM estimates computed by the proposed method depend on the COV of the ones obtained by the NI data. Hence, as the COV of the values computed by averaging NI data increases, the YM estimates computed by the proposed method decrease. Therefore, the proposed model represents an efficient tool to handle actual NI data and to extract reliable information about the mechanical properties of PNC.

Regarding the optimum number of indentations that the proposed model suggests as necessary to obtain reliable estimates of the YM of PNC, there is no obvious optimum grid size based on the results presented in this section. Nevertheless, the collective analysis of the results presented in this chapter shows that the fewer the NI measurements are, the more likely is, from a statistical point of view, to have NI data with larger COV and, thus, the lower the values of the YM computed by the proposed method will be. Moreover, it should be mentioned that the proposed method is intended to be used for modeling of actual experimental NI data. Therefore, taking into account the experimental difficulties encountered in NI experiments, any given array of local YM values can be used to obtain YM estimates using the proposed model.
Chapter 7

Modeling of the Elastic Instability of PNC Structures

Chapter 7 presents one more application of the proposed MSFEM. Specifically, Chapter 7 has two goals. First, it shows the effect of the incorporation of SWCNT in polymers on the elastic stability of thin plates of PNC. The stability analysis is performed by a finite elements (FE) model created in the ANSYS software and calibrated by analytical solutions. Second, the results in Chapter 7 validate the homogenization procedure described in Chapter 4 by showing that the effective Young's modulus and Poisson ratio values computed in Chapter 5 can be used to determine reliably and efficiently the elastic stability of PNC structures with spatially varying random mechanical properties. The numerical results and conclusions presented in Chapter 7 are further supported by a Monte Carlo FE algorithm also created in ANSYS.
7.1 Elastic instability of thin plates

The concept of elastic stability is important in the design and modeling of engineering structures because in many occasions failure is caused by loads which are significantly lower in magnitude than the corresponding material strength. In general, elastic instability, simply known as “buckling,” is observed in structures subject to compressive loads. Hence, buckling occurs when, for a certain “critical” value of the applied loads, two or more equilibrium positions correspond to different deformation modes.

The subject of elastic stability of thin plates has been extensively studied in the literature [27, 103, 113]. However, exact closed-formed solutions exist only for specific geometries and under certain assumptions. In addition, the subject of the stability of thin plates made of materials with random mechanical properties has been only recently investigated [36, 75]. Therefore, the study of the buckling behavior of PNC structures is important in evaluating the role of PNC as structural materials. Section 7.1 presents the fundamental concepts related to elastic stability of thin plates and formulates the plate buckling governing equation (GE) which is subsequently used in the analytical and numerical solutions presented in Chapter 7.

The term “thin plate” is used, as mentioned in Chapter 4, in the case that the in-plane dimensions of a solid plate are larger than the thickness, usually by a factor of 100 or more. For this geometry, the transverse shear deformations, strains and stresses are assumed to be negligible compared to bending deflections. Furthermore, for a thin plate a plane normal to the middle plane is assumed to remain normal after deformation. These assumptions
constitute the so-called classical plate theory (CPT) which is primarily used for elastic, isotropic and homogeneous materials. The effect of plate thickness and shear deformations in the bending of thin plates is described by other theories, such as the Hencky-Mindlin one, which provides more accurate results for “thick plates.”

In the CPT it is possible to represent the deformed state of a plate by a single degree of freedom \( w \) which describes the transverse deflection of the middle plane of the plate. To derive the GE of buckling of a thin plate, the plate element shown in Figure 7.1 is used. Two sets of forces act on this element, as shown in Figure 7.1: in-plane or membrane forces and shears. According to the CPT, the GE of buckling of a plate is given in Equation 7.1.

\[
\frac{\partial^2 M_x}{\partial x^2} - 2\frac{\partial^2 M_{xy}}{\partial x \partial y} + \frac{\partial^2 M_y}{\partial y^2} + (F_x \frac{\partial^2 w}{\partial x^2} + F_y \frac{\partial^2 w}{\partial y^2} + 2F_{xy} \frac{\partial^2 w}{\partial x \partial y}) = 0 \quad (7.1)
\]

In addition, based on the thin plate approximation, the plate element is modeled as a two-dimensional structure. Consequently, by using the plane-stress equilibrium, compatibility and constitutive equations described in Chapter 4, the moments \( M_x, M_y \) and \( M_{xy} \) in Equation 7.1 can be written as functions of the transverse deflection \( w \), as shown in Equation 7.2.

\[
M_x = -D\left(\frac{\partial^2 w}{\partial x^2} + \nu \frac{\partial^2 w}{\partial y^2}\right)
\]
\[
M_y = -D\left(\frac{\partial^2 w}{\partial y^2} + \nu \frac{\partial^2 w}{\partial x^2}\right)
\]
\[
M_{xy} = D(1-\nu)\left(\frac{\partial^2 w}{\partial x \partial y}\right) \quad (7.2)
\]

In Equation 7.2, \( D \) is the plate’s flexural rigidity given in Equation 7.3.

\[
D = \frac{Et^3}{12(1-\nu^2)}, \quad (7.3)
\]
Figure 7.1: The in-plane and shear forces applied to a plate element.
where $E$ is the Young’s modulus, $\nu$ the Poisson ratio and $t$ the plate thickness.

Based on Equations 7.1 and 7.2, the GE of the plate buckling can be written as

$$D\left(\frac{\partial^4 w}{\partial x^4} + 2 \frac{\partial^4 w}{\partial x^2 \partial y^2} + \frac{\partial^4 w}{\partial y^4}\right) - (F_x \frac{\partial^2 w}{\partial x^2} + F_y \frac{\partial^2 w}{\partial y^2} + 2F_{xy} \frac{\partial^2 w}{\partial x \partial y}) = 0 \quad (7.4)$$

Equation 7.4 in conjunction with appropriate sets of boundary conditions (BC) is solved in section 7.2 to compute the buckling loads and modes of simply supported rectangular plates.

### 7.2 Buckling of simply supported rectangular plates

The elastic stability of the thin rectangular plate of Figure 7.2 is examined in this section both analytically and numerically. The agreement between analytical and numerical results shows that the developed FE model in ANSYS can be used to compute accurately and efficiently the buckling loads and modes of thin flat plates subject to various loading and boundary conditions.

#### 7.2.1 Analytical solution

The plate of Figure 7.2 is loaded on the two simply supported edges parallel to the y-axis by the uniformly distributed load $F_x$. The remaining edges (parallel to the x-axis) are also simply supported. Therefore, the BC are

$$w = 0 \quad \text{and} \quad M_x = 0 \quad \text{at} \quad x = 0, \quad \text{and} \quad x = a \quad (7.5)$$

$$w = 0 \quad \text{and} \quad M_y = 0 \quad \text{at} \quad y = 0, \quad \text{and} \quad y = b. \quad (7.6)$$
The critical buckling load in this case can be computed by the Navier solution approach [113]. This solution involves a choice of the form of the transverse deflection of the middle plane of the plate shown in Figure 7.2. Hence, $w$ is represented by the double series shown in Equation 7.7.

$$w = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \alpha_{mn} \sin \frac{m\pi x}{a} \sin \frac{n\pi y}{b},$$  \hspace{1cm} (7.7)

where $\alpha_{mn}$ are parameters to be determined. The coefficients $m$ and $n$ in Equation 7.7 express half-waves of the transverse deflection in the direction of the applied load and the perpendicular one, respectively. Substitution of Equation 7.7 in Equation 7.4 and imposition of the BC yields

$$F_x = \frac{\pi^2 a^2 D}{m^2} \left( \frac{m^2}{a^2} + \frac{n^2}{b^2} \right)^2.$$  \hspace{1cm} (7.8)
To derive Equation 7.8, all coefficients $\alpha_{mn}$ in Equation 7.7 except one were set equal to 0. The remaining coefficient was set equal to 1.

Given Equation 7.8, the critical load for a given rectangular plate is obtained by a specific combination of $m$ and $n$ values. In the case of the uniaxially compressed plate of Figure 7.2, the plate buckles in such a way that there can be several half-waves in the direction of the applied load but only one in the perpendicular direction. Hence, the critical load in this case is obtained when $n = 1$. In this case, Equation 7.9 shows the critical buckling load of the rectangular plate of Figure 7.2.

$$F_{x,cr} = \frac{\pi^2 D}{a^2} \left( m + \frac{\mu^2}{m} \right)^2$$  \hspace{1cm} (7.9)

In Equation 7.9, $\mu = a/b$ is the aspect ratio of the in-plane dimensions. For $m = \mu = 1$, the critical load is equal to

$$F_{x,cr} = \frac{4\pi^2 D}{b^2}.$$  \hspace{1cm} (7.10)

Timoshenko and Gere [103] showed that depending on the value of $m$, the critical buckling load is obtained by using Equation 7.9 for $m = \mu$, which leads always to the value given by Equation 7.10. The corresponding modes involve exactly $m$ half-waves of transverse deflection in the direction of the applied load.

### 7.2.2 Numerical solution

The elastic stability of the thin plate shown in Figure 7.2 is investigated in this section by a FE model created in ANSYS. To compute the buckling loads and modes using the numerical model, an eigenvalue problem is formulated and solved. A brief description
of the procedure followed in the numerical model is presented next and is based on the calculation of buckling loads using FE, presented by Cook et al. [13].

The first step in numerically computing buckling loads with FE is to apply an arbitrary reference set of loads on the structure and to determine the resulting stress field by performing a standard static FE analysis, similar to the one described in Chapter 4. In the case of thin structures, such as the plate of Figure 7.2, the lateral deflection is affected by the existence of membrane forces which are tangent to the middle plane of the plate. These membrane forces increase the in-plane stiffness of the plate and must be taken into account when computing buckling loads. The increase of the plate's stiffness caused by membrane forces is quantified by the so-called geometric stiffness matrix (GSM), which in the case of rectangular plates is given in Equation 7.11

\[
[K_\sigma] = \int \int [M]^t \begin{bmatrix} F_x & F_{xy} \\ F_{xy} & F_y \end{bmatrix} [M] dx dy, \quad (7.11)
\]

where \([K_\sigma]\) is the GSM, \(F_x, F_y, F_{xy}\) are the in-plane forces shown in Figure 7.1 and \([M]\) is defined in Equation 4.73 as a matrix of shape functions used in the FE analysis to compute strains based on nodal displacements. From Equation 7.11 it can be concluded that the GSM is independent of the material properties while it depends on the element's geometry and the displacement field. Moreover, for a given reference set of applied loads \(\{F\}^\text{ref}\) there is a corresponding GSM equal to \([K_\sigma]\), while for a set of loads which is \(\lambda\) times the reference one, i.e.

\[
\{F\} = \lambda \{F\}^\text{ref}, \quad (7.12)
\]
the GSM is given in Equation 7.13

\[
[K_\sigma] = \lambda [K_\sigma]_{ref}.
\] (7.13)

In the case that linear material behavior is assumed, as in the CPT, the stiffness matrix of the structure remains unchanged for an increase in the applied loads. Therefore, at the critical buckling load \( \lambda_{cr} \{ F \}_{ref} \) a bifurcation of equilibrium positions occurs and

\[
([K] + \lambda_{cr}[K_\sigma]_{ref}) \{ D \}_{ref} = \lambda_{cr} \{ F \}_{ref}
\] (7.14)

\[
([K] + \lambda_{cr}[K_\sigma]_{ref}) \{ D_{ref} + \delta D \} = \lambda_{cr} \{ F \}_{ref}
\] (7.15)

where \( \{ \delta D \} \) are the buckling and \( \{ D \}_{ref} \) the displacements for the reference set of loads. Subtraction of Equation 7.15 from Equation 7.14 yields

\[
([K] + \lambda_{cr}[K_\sigma]_{ref}) \{ \delta D \} = \{ 0 \}
\] (7.16)

Equation 7.16 is an eigenvalue problem. Its eigenvalues are the buckling loads and its eigenmodes are the corresponding buckling modes. In fact, the smallest eigenvalue is the critical buckling load.

To determine the accuracy and efficiency of the numerical model in computing the buckling loads and modes of a thin plate similar to the one presented in Figure 7.2, a material is assumed with Young’s modulus and Poisson ratio equal to 2.026 GPa and 0.3, respectively. The in-plane dimensions of the plate are equal to 1 and the thickness is set equal to 0.01. For this particular choice of material properties and geometry, the critical buckling load for \( m = 1, 2, 3, 4 \) is computed by using Equation 7.10 and is found equal
Figure 7.3: Above: Comparison of the numerical solution for the critical buckling load of the plate of Figure 7.2 with the analytical solution. Below: Corresponding error.

to 7324 Pa. Figure 7.3 compares the analytical and the numerical solution as a function of the total number of finite elements used in the model. As seen in Figure 7.3, the error in the numerical solution is less than 1% even for a FE mesh of 10x10. Therefore, it is concluded that the numerical model is capable of computing accurately and efficiently (the computational time is less than two seconds) the buckling loads of thin plates subject to specific loading and boundary conditions.
In addition, Figure 7.4 shows the first four buckling modes for a thin plate similar to the one presented in Figure 7.2. To obtain these modes using the numerical model, four values of the aspect ratio of the in-plane dimensions equal to 1, 2, 3 and 4 were used to retrieve the analytical solution in Equation 7.9. As seen in Figure 7.4, the first buckling mode computed by the FE model consists of one half-wave of the transverse deflection in the direction of the applied load, exactly as the analytical solution predicts. Similarly, the second mode consists of two, the third one of three and the fourth of four half-waves. Consequently, the buckling modes computed by the FE model agree with the analytical solution.

Figure 7.4: The first four buckling modes of the simply supported thin flat plate shown in Figure 7.2.
7.3 Buckling of PNC structures

This section successfully determines the effect of the incorporation of SWCNT in polymers on the elastic stability of a thin plate model. Furthermore, this section shows the effect of the homogenization procedure performed by the proposed MSFEM on the computed buckling loads. A pertinent Monte Carlo study based on an algorithm created in ANSYS is used to support the results of this section.

Figure 7.5 shows the plate model used in the numerical solution. The BC for this particular model are

\[
\begin{align*}
w &= 0 \quad \text{at} \quad x = 0, 1 \quad \text{and} \quad y = 0, 1 \quad (7.17) \\
v &= 0 \quad \text{at} \quad y = 0 \quad (7.18) \\
u &= 0 \quad \text{at} \quad x = y = 0 \quad (7.19)
\end{align*}
\]

where \( u, v \) are the lateral displacements in the \( x \) and \( y \) directions, respectively. The uniformly applied load \( P \) is set equal to 1 to perform the buckling analysis in ANSYS.

Figure 7.6 shows the first four buckling loads for the plate of Figure 7.5. As seen in Figure 7.6, the incorporation of SWCNT in polymers causes an increase in the buckling loads. This behavior of the buckling loads is a result of the higher Young’s modulus of PNC with respect to the polymers. The loads shown in Figure 7.6 were computed by using the Young’s modulus and Poisson ratio values for the two polymers presented in Chapter 5 and the corresponding effective values computed by the MSFEM for a 10x10 mesh. The FE model in ANSYS also consists of a 10x10 mesh, since it was shown in section 7.2.2
Figure 7.5: The square thin plate of PNC numerically modeled to study the effect of random material properties on the elastic stability.

that the error for this mesh size is insignificant with respect to larger ones.

Figure 7.7 shows the corresponding four buckling modes for the plate of Figure 7.5. The first three modes in this case are similar to the ones presented in Figure 7.4. The difference in the fourth mode is explained by the different set of boundary conditions imposed on the two plate models.

To evaluate the effect of the values for the Young's modulus and Poisson ratio computed by the proposed MSFEM in Chapter 5 on the buckling loads shown in Figure 7.6, a Monte Carlo FE algorithm was created in ANSYS. This algorithm computes 500 times the buckling loads for the thin plate shown in Figure 7.5 in which the Young's modulus and the
Figure 7.6: The first four buckling loads for the PNC modeled in Chapter 5, as well as the corresponding polymers. The Figure shows that the incorporation of SWCNT in polymers causes an increase of the buckling loads.

Figure 7.7: The first four buckling modes of the plate shown in Figure 7.5.
Poisson ratio are random. The Mori-Tanaka homogenization method in conjunction with the random field model both developed in Chapter 4 are used to generate samples of the two material properties needed in the FE solution. Each finite element in the solution is assigned a pair of values for the Young’s modulus and the Poisson ratio from the generated samples. The statistical analysis of the ensemble of numerically computed buckling loads in the Monte Carlo algorithm are subsequently used to compute the mean value and coefficient of variation of the four buckling loads for all PNC.

Therefore, Figure 7.8 shows that the effective values for the Young’s modulus and the Poisson ratio yield buckling loads which perfectly agree with the mean values computed by the Monte Carlo algorithm. This agreement validates the use of the effective properties computed by the MSFEM in meso-/macroscale modeling.

Furthermore, Figure 7.9 shows the coefficient of variation (COV) for the four buckling loads computed by the ensemble of Monte Carlo results. For all PNC, the COV is less than 2% which implies a weak dependence of the buckling loads on the random mechanical properties of the PNC. However, the effective values for the PNC properties computed by the proposed MSFEM are capable of reliably providing the buckling loads of structures with random properties, as shown in this section.

In summary, the elastic stability of PNC structures was successfully examined in Chapter 7. The results presented in section 7.3 show that the incorporation of SWCNT in polymers causes an increase of the buckling loads. Furthermore, in the case that the material properties of PNC structures are assumed to be random, the effective values for the Young’s
Figure 7.8: The first four buckling loads for the plate model having the mechanical properties of the PNC modeled in Chapter 5, as well as the corresponding loads computed by the Monte Carlo algorithm for the plate model with random properties. The Figure shows that the use of the effective values for the YM and PR computed by the proposed MSFEM yields reliable estimates of the buckling loads of PNC structures with random material properties.

Figure 7.9: The coefficient of variation of the first four buckling modes of the plate model in Figure 7.5 with random mechanical properties. The Figure shows a weak dependence of the buckling loads on the random material properties.
modulus and the Poisson ratio computed by the proposed MSFEM can be used to determine reliably the buckling loads and modes.
Chapter 8

Concluding remarks

This dissertation has introduced a new multiscale stochastic finite elements method (MS-FEM) for determining the mechanical properties of polymer nanocomposites (PNC) consisting of polymers reinforced with single-walled carbon nanotubes (SWCNT). Methods reported in the literature that provide estimates for the mechanical properties of PNC are often based on assumptions and approximations that lead to discrepancies when compared to corresponding experimental findings. The proposed method yields reliable estimates of the mechanical properties of PNC by using actual experimental characterization evidence and by developing a hierarchical and stochastic multiscale method. The effectiveness and robustness of the proposed method have been validated in this dissertation by modeling two different kinds of experimental data which correspond to tensile and nanoindentation testing. Further validation of the results of the proposed method is provided by modeling of the elastic stability of PNC structures.
The proposed MSFEM has been based on actual characterization evidence which shows that, contrary to previously made assumptions in the literature, the dispersion of SWCNT in polymers is not uniform. Hence, the proposed method has shown that heterogeneities related to the non-uniform SWCNT dispersion in polymers cause variations in the local mechanical properties that affect the overall mechanical behavior of PNC. Therefore, local information about the material structure and properties of PNC has been modeled and quantified in this dissertation to reliably determine their overall mechanical behavior.

Specifically, Chapter 3 has shown that actual images of the structure of PNC reveal the existence of a number of SWCNT formations at the nano-/microscale, such as bundles or ropes, clusters and agglomerates. Consequently, it has been argued in Chapter 3 that the assumption of uniform/homogeneous dispersion of SWCNT in polymers cannot be made a priori and without the support of appropriate and detailed analysis of the experimental characterization evidence. Chapter 3 has further suggested that to determine the mechanical properties of PNC, realistic assumptions about the actual shape, size, orientation and dispersion distributions of the SWCNT in polymers must be made. Such assumptions lead to accurate and reliable modeling of the macroscopic mechanical behavior of PNC based on information that spans the range from nano to micro scale. The method presented in this dissertation answers fundamental questions related to the way that nanoscale information can be successfully transferred to higher length scales when modeling the mechanical behavior of PNC.

Chapter 4 has presented the MSFEM used for characterization and modeling of PNC.
Hence, this chapter shows that PNC are random heterogeneous media and, consequently, that their modeling should reflect their nature. Therefore, randomness in PNC has been identified in Chapter 4 both in terms of the overall material properties and the nano-/microstructure. Hence, it has been suggested that the existence of heterogeneities in the PNC structure causes non-uniform phenomena such as fluctuations in the local mechanical properties. These local properties are linked to the overall mechanical behavior using the proposed MSFEM.

In the developed method, an appropriate material region (MR) is defined as a reference volume element in which estimates for the mechanical properties of PNC are computed. In this MR, the proposed MSFEM identifies, models and quantifies randomness at the nanoscale. Specifically, the local SWCNT volume fraction (VF) is used as a suitable descriptor at the nanoscale which quantifies the local variations observed in the dispersion of SWCNT in polymers. Therefore, local SWCNT VF values in a defined grid of points in the MR have been modeled in Chapter 4 by random variables (RV) that have specific probability density functions (PDFs). To theoretically support this model, the MSFEM defines this set of RV as a discretization of a two-dimensional, continuous and homogeneous random field (RF). This RF discretization has been further used by the MSFEM to discretize the MR in a number of finite elements (FE). By choosing a specific discretization scheme of the RF of SWCNT VF values and by using this discretization in a FE method a stochastic finite elements method has been formulated in Chapter 4.

To account for variations in the actual dispersion of SWCNT in polymers, a popu-
lation of realizations of the random vector which includes values for the local SWCNT VF has been numerically generated, taking into account the physical meaning of the VF and using pertinent experimental information. Based on the local SWCNT VF values, the proposed MSFEM computes local material properties of PNC by using an agglomeration model in combination with a Mori-Tanaka (MT) homogenization method. Therefore, the randomly dispersed heterogeneities in the MR are modeled by a two-phased material in which SWCNT are partially dispersed in the polymer and agglomerated in the form of spherical inclusions. Pertinent indices defined in Chapter 4 quantify the number of SWCNT in the two phases and are subsequently incorporated in the MT method to compute the local mechanical properties of PNC.

The MT homogenization that has been used in the proposed MSFEM to determine the mechanical properties of PNC takes under consideration the effect of the SWCNT VF, aspect ratio, shape, agglomeration, dispersion and material properties. Regarding the material properties of SWCNT, the proposed method uses a multiscale model reported in the literature which includes the polymer-CNT interaction. This model provides realistic estimates of the material properties of SWCNT. These properties have been subsequently incorporated in the proposed MSFEM to determine the effective mechanical properties of PNC.

In Chapter 5, estimates for the Young's Modulus (YM) and Poisson Ratio (PR) of two PNC studied in the literature have been computed and compared with pertinent experimental findings. The computed estimates were obtained by solving a specific static problem
which involves a thin plate subject to tensile loading. The PNC that have been modeled in this dissertation were chosen because important characterization information about their fabrication, structure and mechanical properties have been reported in the literature. This information has been used by the proposed method to determine the values of important parameters, such as the SWCNT aspect ratio, VF, agglomeration, orientation distribution and bonding. In addition, the mechanical properties of the PNC modeled in Chapter 5 have been also determined by tensile tests experiments, and these findings are used to calibrate parameters in the proposed MSFEM.

The derived results for the mechanical properties of PNC by the proposed MSFEM in Chapter 5 have shown that the numerical values of the YM of the PNC are significantly different from the ones obtained by direct application of the MT homogenization method; they further agree with pertinent experimental findings. In contrast, the corresponding PR values have been found to be only slightly different that the ones computed by the MT method and not significantly different than the polymer PR values. Consequently, Chapter 5 has shown that the direct application of the MT method for determining the mechanical properties of PNC does not furnish reliable estimates. However, the MSFEM has proved to be flexible enough to incorporate experimental information and to yield YM estimates which in some cases are less than 1% different from the corresponding experimental ones. To achieve this kind of agreement between modeling and experimental values, the effect of a number of parameters on the derived results has been examined in Chapter 5. Specifically, it was found that the choice of the PDF for the random SWCNT VF values, as well as their
standard deviations affect the results of the proposed MSFEM.

Chapter 5 has further shown the effect of the number of FE on the computed values for the YM and PR of PNC. Specifically, it was observed that by increasing the number of FE, both the mean value and the standard deviation of the estimates computed by the proposed MSFEM decrease. This fact shows that the finite dimensions of the domain defined by the MR create a scale dependence on the results. However, by using the MSFEM, the local mechanical properties have been determined based on a multiscale homogenization procedure which decreases the coefficient of variation (COV) of the determined mechanical properties. Consequently, the uncertainty in the computed values also decreases. This behavior of the COV shows the robustness of the proposed method.

Chapter 6 has presented a second application of the proposed MSFEM. Specifically, experimentally obtained nanoindentation (NI) data are recognized in Chapter 6 as measurements of the local YM values of PNC. Therefore, it is suggested that to determine the effective YM of PNC the proposed method could be used since it yields reliable estimates of the effective YM based on information about the local material properties. This application aims to rectify existing problems in determining the YM of PNC based on NI measurements.

In Chapter 6, numerically generated NI data, which are compatible with reported experimental ones, have been used to determine the YM of PNC. The generation of NI data was based on the random field model and the MT homogenization method presented in Chapter 4, as well as an application of the spectral representation method in two-dimensions.
The numerically generated NI data were subsequently used in the Monte Carlo FE part of the proposed MSFEM. The results in Chapter 6 show that the computed YM estimates are lower than the corresponding ones obtained by direct averaging of the NI data. This discrepancy is indicative of the success of the proposed method. Furthermore, it has been observed in Chapter 6 that the COV of the NI data is in all cases higher than 10%, while the proposed MSFEM yields YM values that have a COV almost equal to zero. Hence, Chapter 6 has demonstrated that even if the mean value of the local YM estimates obtained by direct averaging of NI data is close to the YM measured by tensile tests, the corresponding standard deviation is such that the direct averaging approach is unreliable. In contrast, the proposed method has succeeded in providing estimates which agree with other experimental findings, and they additionally have smaller standard deviations than the ones computed by direct averaging.

Furthermore, a careful comparison of the YM estimates and their COV has revealed an interesting correlation between these two parameters. Specifically, it is concluded in Chapter 6 that the higher the COV of the NI data is, the lower the YM estimates computed by the proposed method are compared to the corresponding values obtained by direct averaging of the NI data. Physically, this result has been found to be meaningful. Specifically, it is true that if all indentations lead to local YM values which do not present significant variations, then their standard deviation is expected to be small, and, therefore, the mean value obtained by direct averaging must be close to the overall YM of the PNC. However, in the case of significant variations in the NI data, the mean value obtained by direct aver-
aging can be different compared to pertinent findings. In this case, the effect of the spatial randomness in the local mechanical properties is more important.

In addition, Chapter 6 has examined the correlation between the number of FE, i.e. the number of indentations, with the computed YM estimates. The presented results did not show a clear trend with increasing FE mesh size. Nevertheless, it has been realized that the proposed method can yield reliable estimates for any number of indentations.

Chapter 7 has presented an additional application of the proposed MSFEM. Specifically, the values for the effective mechanical properties of PNC computed in Chapter 5 were used to quantify the effect of the incorporation of SWCNT in polymers on the elastic stability or buckling of PNC structures. Therefore, Chapter 7 presents the fundamental concepts and governing equations of the buckling of thin plates. These equations were solved both analytically and numerically to compute the critical buckling loads and modes of thin rectangular plates of PNC subject to various boundary conditions. The numerical solution was obtained by a FE model created in the ANSYS software. Analytical and numerical results were found in good agreement. The computed results show that the incorporation of SWCNT in polymers causes an increase of the buckling loads because of the higher YM values of the PNC compared with the polymer ones.

Furthermore, a Monte Carlo FE model also created in ANSYS has been used in Chapter 7 to investigate the effect of the spatial randomness in the local material properties of PNC on the elastic stability of their structures. The results for the buckling loads and modes obtained for a thin plate model with random material properties were compared with the
corresponding loads computed by using the effective values for the YM and PR. This comparison showed that the computed effective values by the proposed MSFEM can be reliably used in modeling of the mechanical behavior of PNC structures in the meso-/macroscale. This conclusion was drawn from the fact that the buckling loads computed by the Monte Carlo FE algorithm were in excellent agreement with the ones computed by using the effective values for the mechanical properties of PNC. Hence, it is argued in Chapter 7 that the proposed MSFEM can be used to reliably and efficiently model the elastic stability of structures with random material properties.

The multiscale method presented in this dissertation has shown that the effect of spatial randomness on the effective mechanical properties of PNC is an important parameter which should be taken under consideration when modeling the mechanical behavior of nanocomposite materials. However, the proposed method could be further enhanced by direct image analysis information. Specifically, existing image analysis methodologies are capable of providing explicit information about the exact aspect ratio distribution of SWCNT in other materials, as well as about the local SWCNT VF values. The incorporation of these two parameters into the proposed method would permit an even more realistic description of the role of spatial randomness in the mechanical behavior of PNC.

Regarding the multiscale nature of the proposed method, it should be noted that although the structure of the method, as presented in this dissertation, is hierarchical, a concurrent multiscale method could also be formulated. For example, the consideration of the sub-element structure in a material domain, which is defined by an actual image of
the structure of PNC, permits the simultaneous use of molecular dynamics (MD) simulations and FE methods. Hence, local material properties of appropriately defined “RVEs” could be computed by MD. Subsequently, this information could be used in a FE method to determine the mechanical properties of PNC at the macroscale.

Furthermore, the use of local information, such as the SWCNT VF or the direct measurement of the YM of PNC, could also be used to develop other stochastic finite elements methods that would require less computational time compared with the hundreds of iterations involved in Monte Carlo simulations. For example, knowledge of the statistics of the two-dimensional material random fields allows the use of spectral methods, such as the Karhunen-Loeve expansion. In spectral methods, unlike the Monte Carlo methods, the FE formulation is modified to include the effect of material randomness. However, spectral methods provide results which could only be obtained by hundreds of Monte Carlo type simulations. Hence spectral methods offer more advantages in multiscale methods and the author of this dissertation is already working towards the use of such methods for modeling of nanocomposite materials.

In addition, as mentioned in this dissertation, it should be noted that reliable modeling of PNC begins with the reliable determination of the mechanical properties of their constituents. In this context, it is true that many models suggested in the literature either ignore or average the effect of defects in the structure of SWCNT on their mechanical properties. Therefore, values proposed in the literature often overestimate the actual reinforcement role of SWCNT, as observed by comparing pertinent experimental and modeling results.
Therefore, work in determining the realistic mechanical properties of PNC is proposed to determine the actual reinforcement capabilities of SWCNT.

Collectively, this dissertation has shown that PNC are random heterogeneous materials because of the non-uniform dispersion of SWCNT in polymers. Therefore, it has presented a complete methodology on how the structure of PNC at the nanoscale should be used to create a realistic model for determining the mechanical properties of PNC.

Concluding, it should be noted that the existence of clusters, agglomerates and bundles affects the mechanical properties of PNC in a way that assumptions, such as straight SWCNT and good SWCNT-polymer interface are perhaps valid only in the area around each individual SWCNT. Hence, as long as the fabrication techniques used to produce PNC do not succeed in creating “long” nanofibers or in achieving true homogeneous dispersion of “short” nanotubes, local phenomena and randomness will continue to affect the mechanical properties of nanocomposites. Consequently, the proposed MSFEM, its future extensions and possible similar stochastic approaches will provide invaluable information in understanding the mechanical behavior of PNC at the micro-/meso-/ and macroscales.
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