FINITE ELEMENT MODELING OF CARBON NANOTUBE REINFORCED POLYMER COMPOSITES AND EVALUATING ITS THERMAL CONDUCTIVITIES

by

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ABSTRACT

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High thermal conductivity of carbon nanotubes has motivated us to study and understand the thermal mechanisms in nanocomposites. Though several theoretical models predict a high thermal conductivity for CNT reinforced polymer composites, the experimental validation are not so encouraging. A finite element model of MWNT reinforced nanocomposite is developed based on continuum mechanics approach. The finite element model is a representative volume element (RVE) with single MWNT inclusion. The inclusion is modeled based on the continuum model of MWNT as

effective solid fiber [22].The interface resistance between the nanotube and the matrix material is modeled using thermal contact elements. The finite element analysis was carried out keeping volume fraction of MWNT fibers as constant and varying three important parameters which influences the effective thermal conductivity. Analysis with varying volume fractions of CNT fibers was also carried out to study the influence of volume fraction. The results obtained were in agreeable range with the theoretical calculations made based on the work of Bagchi and Nomura [22]. The effective thermal conductivity of MWNT reinforced nanocomposites with MWNTs of high aspect ratios showed gradual increase in conductivity with increase in length while it showed a drastic decrease in effective thermal conductivity with increase in the diameter of the MWNT inclusion. The finite element analysis showed that the interface resistance between the nanotube and the matrix material does not affect effective thermal conductivity noticeably which is contradictory with few theoretical models which attribute interface resistance for lower than expected effective thermal conductivity. The analysis predicts linear increase of effective thermal conductivity with increase in volume fraction of the MWNT fibers in matrix material; this is also in accordance with the theoretical model. The above analysis also validates the use of finite element approach based on continuum mechanics in studying the overall behavior of the nanocomposites.

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CHAPTER 1

INTRODUCTION

1.1 Introduction to composite materials

With our continuing quest for lighter and stronger composites, the demand for new types of composite materials is increasing. In recent years various composite materials have been used extensively in aircraft structures, space vehicles, automobiles, sporting goods, electronic packaging to medical equipment, and many consumer products. The main advantage of composite materials is the potential for a high ratio of stiffness to weight, corrosion resistance, high fatigue strength etc…

A composite material consists of one or more bonded discontinuous phases distributed in one continuous phase. The discontinuous phase which is also called as the reinforcement phase or fillers has enhanced material properties than the continuous phase called as matrix. The properties of a composite material are a result of material properties of constituent materials, their geometric distribution and their interactions. The concentration of the reinforcement is usually measured by the volume fraction or by the weight fraction. The concentration of the reinforcement is a determining parameter of the properties of the composite material. For a given concentration, the distribution of the reinforcement in the volume of the composite is also an important parameter. A uniform distribution will ensure "homogeneity" of the material *i.e.* the properties of a composite will be independent of the point of measurement. In the case of a non-uniform distribution of the reinforcement, fracture of the material will be initiated in the zones which have less reinforcement and hence weakening the strength of the composite. In case of composite materials in which the reinforcement is made of fibers, the orientation of the fibers determines the anisotropy of the composites material.

Composites are broadly classified as fiber composites and particles composites. If the reinforcement is in the form of fibers, the composite material is called as a fiber composite. The fibers used may be continuous, discontinuous, chopped fibers, short fibers, etc… Particulate composites are made of particle reinforcement materials. Particles are generally used to improve certain properties of the materials such as stiffness, behavior with temperature, resistance to abrasion, decrease of shrinkage, etc. Composites are also classified based on the nature of the constituents as organic matrix composites, metallic matrix composites and mineral matrix composites (ceramic). The most common advanced composites are polymer matrix composites (PMCs) consisting of a polymer reinforced by fibers. The most common fibers used are glass, carbon, Kevlar, silicon carbide (SiC), boron, aluminum etc…

1.2 Carbon nanotubes and Nanocomposites

Substantial developments have been made during the last few years in the field of nano composites. Nanocomposites are composite materials with at least one of nanocomposites phases with one or more dimensions like length, width, thickness in the nanometer range *i.e.* 1 to 100 nm. This is the range where phenomena associated with atomic and molecular interactions strongly influence the macroscopic properties of the materials. It is well-known that molecular forces bonding the interaction between the interfaces, and the physical phenomena occurring at this level will dictate the aggregate properties of materials. Carbon nanotubes are being proved to be an efficient reinforcement in nanocomposite materials for various applications. In 1991, Iijima obtained transmission electron micrographs of elongated carbon nanoparticles that appeared to consist of cylindrical graphitic layers capped on ends with fullerene-like domes [1]. In 1992 Ajayan and Ebbesen succeeded in making macroscopic quantities of carbon nanotubes [2]. Synthesis of carbon nanotubes is done using several techniques such as carbon-arc discharge method, laser ablation method, chemical vapor deposition (CVD) method, flame synthesis, and Smalley's high-pressure carbon monoxide (HIP-CO) process. Producing aligned CNTs with control over the diameter and uniformity in length of the CNTs is a challenging task.

1.3 Properties of CNTs and CNT nanocomposites

Carbon nanotubes are one of the strongest materials known to humans, both in terms of the tensile strength and elastic modulus. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, an MWNT was tested to have a tensile strength of 63 GPa [3]. CNTs also have very high elastic moduli, on the order of 1 Tpa . Since carbon nanotubes have a low density for a solid of 1.3-1.4 g/cm^3, its specific strength is the best of known materials. Polymer based composites reinforced with a small percentage of CNTs can significantly improve the mechanical, thermal, and barrier properties of polymer matrix material. Nanotubes are currently being commercialized in applications where conductivity and other material characteristics need to be enhanced.

Significant development has been made in CNT composite materials. Their remarkable properties offer the potential for fabricating composites with substantially enhanced physical properties including conductivity, strength, elasticity, and toughness. Effective utilization of CNT in composite applications is dependent on the homogeneous distribution of CNTs throughout the matrix. Polymer-based nanocomposites are being developed for electronics applications such as thin-film capacitors in integrated circuits and solid polymer electrolytes for batteries. Research is being conducted throughout the world targeting the application of carbon nanotubes as materials for use in transistors, fuel cells, big TV screens, ultra-sensitive sensors, high-resolution AFM probes, supercapacitor, transparent conducting film, drug carrier, catalysts, and composite material.

1.4 Thermal conductivity in CNT composites

The problem of heat transfer in composites filled with fibers has been extensively studied for decades. The main parameters affecting the thermal properties of composites are the volume fraction, aspect ratio, alignment of the fibers, and the adhesion between the fibers and the matrix, and the thermal property of the interface. Theoretical estimates show that an increase in the aspect ratio of highly conducting fibers would dramatically increase the thermal conductivity of the composite. Based upon this consideration, graphite fibers are frequently used in industry to improve thermal conduction of composites because of their high thermal conductivity [4].

Conducting experiments for material characterization of the nanocomposites is a very time consuming, expensive and difficult. Many researchers are now concentrating on developing both analytical and computational simulations. Molecular dynamics (MD) simulations are widely being used in modeling and solving problems based on quantum mechanics. Using Molecular dynamics it is possible to study the reactions, load transfer between atoms and molecules. If the objective of the simulation is to study the overall behavior of CNT-based composites and structures, such as deformations, load and heat transfer mechanisms then the continuum mechanics approach can be applied safely to study the problem effectively

Many papers have been published on the behavior of the nanocomposites using Molecular dynamics simulations (Huxtable *et al*. [5]). The MD simulation conducted by Shenogin [4] showed that the thermal interface resistance is one of the influencing factors for the thermal conductivity of carbon-nanotube polymer composites and organic suspensions. . X.L. Chen *et.al* [6]has conducted finite element analysis for determining effective mechanical properties of CNT based nanocomposites using square representative volume element. He has reported that the addition of long CNTs in composite can increase the stiffness of matrix material by 33% in axial direction and is consistent with the current literature.

In this thesis, a finite element model of a CNT composite has be developed using the Representative volume element (RVE) to evaluate the effective thermal conductivity of the CNT polymer composite material. This model is based on the principles of continuum mechanics. The interface has been modeled using contact elements. The CNT is considered to be rigid in the matrix material. The results obtained were agreeable with the theoretical values.

This thesis is divided in to following chapters. Chapter 2 mainly deals with material properties and various processes for synthesising CNT composite materials. Chapter 3 deals with the finite element modeling of CNT composite using the representative volume element. Chapter 4 is dedicated to the results and data interpretation. Chapter 5 gives the conclusions and scope for future work.

CHAPTER 2

CARBON NANOTUBE COMPOSITES

2.1 Introduction

This chapter deals with various kinds of nanotubes and fullerenes. It is important to have a better understanding of the material properties of CNTs in order to effectively utilize them in a composite. Different synthesis processes for both carbon nanotubes and their composites with the ongoing research and challenges have been addressed. A brief overview on the material properties of CNT based nanocomposites presented in this chapter.

2.2 Structure of Carbon Nanotubes and C-60

The research and development of carbon-based fullerene and carbon nanostructures have led to the discovery of C60 and carbon nanotubes. Bucky ball C60 is the third major form of pure carbon next to graphite and diamond. C60 molecules & buckminsterfullerene have 60 carbon atoms consisting of truncated icosahedrons, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. In a C_{60} molecule, a carbon atom is present at each vertex of this structure and has all valences satisfied by two single bonds and one double bond [7]. It was discovered in 1985 by Dr. Richard E. Smalley and group from Rice University [7] and is named after famous American architect, R. Buckminster Fuller.

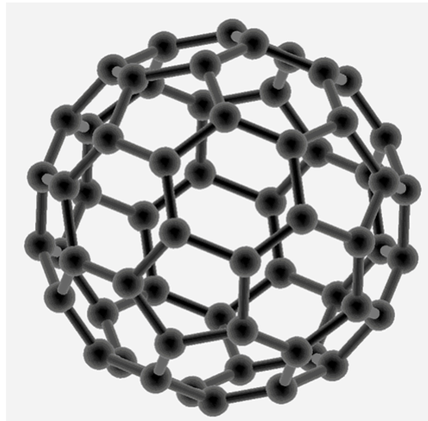

Figure 2.1: Buckminsterfullerene or C-60 molecule

Carbon nanotubes which are long, thin cylinders of carbon were discovered in 1991 by S. Iijima [1]. These are large macromolecules that are unique for their size, shape, and remarkable physical properties.

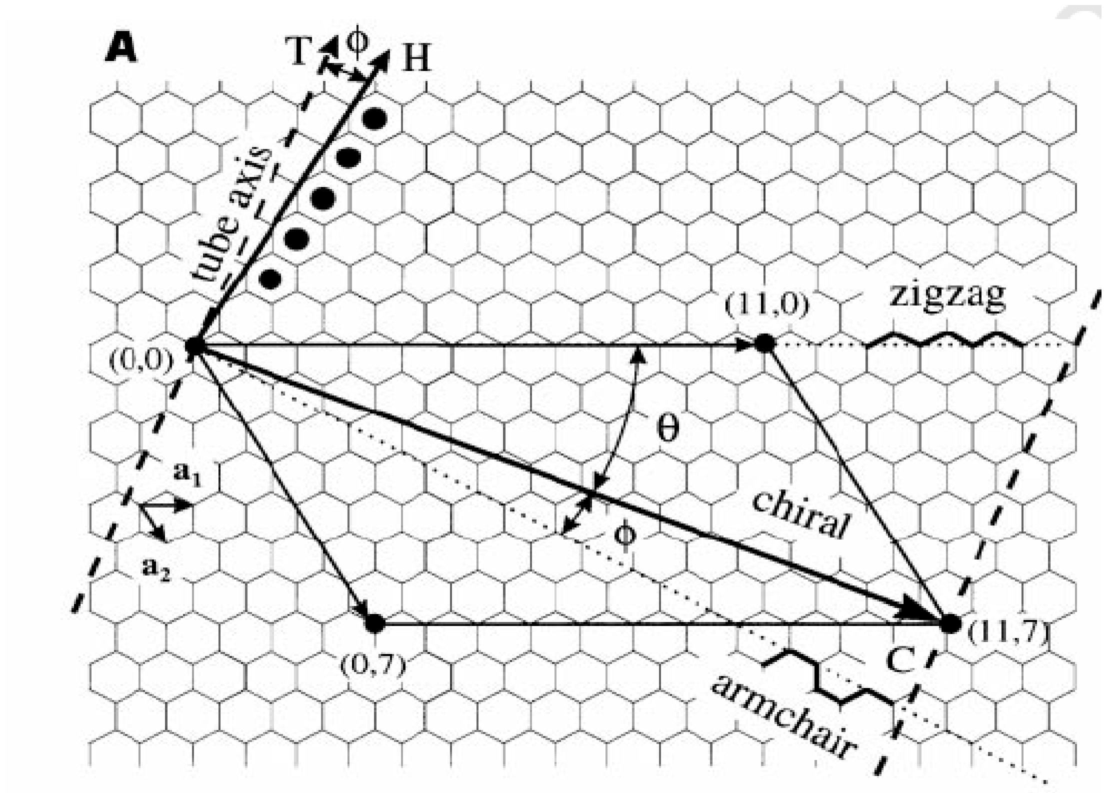

Figure 2.2: Relation between the hexagonal carbon lattice and the chirality of carbon nanotubes [8].

A single SWNT can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into an endless cylinder. By rolling up the sheet along the vector C, the origin (0, 0) coincides with point C, and a nanotube indicated by indices (11, 7) in figure 2.2 can be formed. If the sheet is rolled along the dotted line it will result in forming CNTs that are zigzag or armchair. All other wrapping angles lead to chiral tubes whose wrapping angle is specified relative to either the zigzag direction (v) or to the armchair direction. Dashed lines are perpendicular to C and run in the direction of the tube axis indicated by vector T. The solid vector H is perpendicular to the armchair direction and specifies the direction of nearest-neighbor hexagon rows indicated by the black dots. The angle between T and H is the chiral angle ϕ [8]. Atomically resolved images of scanning tunneling microscopy (STM) of single-wall carbon nanotubes is shown in figure 2.3.]. In the figure 2.3 the chiral angle $\phi = 7°$, and diameter d = 1.3 nm of tube no. 10 correspond to vector $C = (11, 7)$.

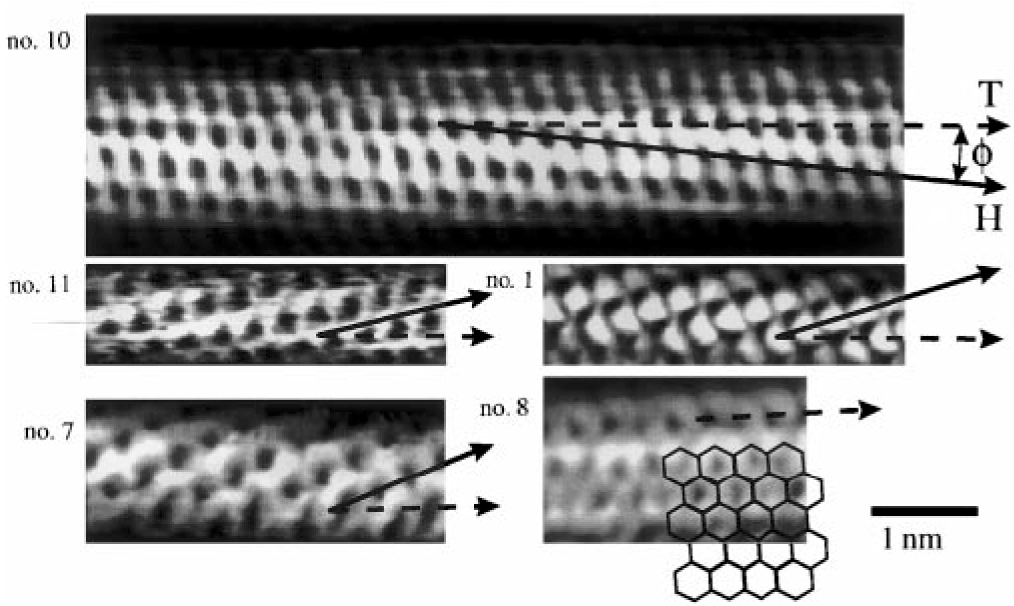

Figure 2.3: Shows atomically resolved STM images on five different tubes [8].

Carbon nanotubes can be constructed by wrapping up a single sheet of graphite such that two equivalent sites of the hexagonal lattice coincide. The wrapping vector, **C**, which defines the relative location of the two sites, is specified by a pair of integers (n, m) that relate **C** to the two unit vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$ and is given by the following equation [8].

$$\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2. \qquad (2.1)$$

A tube is called “armchair” if n equals m, as shown in figure 2.3 image no.8. and “zigzag” in the case $m = 0$ as shown in fig 2.3 image no 8. All other tubes are of the "chiral" type and have a finite wrapping angle ϕ with 0° < ϕ < 30°. The armchair ($n = m$) tubes have bands crossing the Fermi level and are therefore metallic. For all other tubes (chiral and zigzag) there exist two possibilities. When $n - m = 3l$ (where l is an integer), tubes are also expected to be metallic. In the case $n - m \neq 3l$, tubes are predicted to be semiconducting with an energy gap of the order of ~0.5 eV. This gap should only depend on the diameter, that is, $E_{gap} = 2\gamma_0 a_{C-C}/d$, where γ_0 is the C–C tight-binding overlap energy, a_{C-C} the nearest-neighbor C–C distance (0.142 nm) and d the diameter [8].

There are two main types of carbon nanotubes, multi-walled nanotubes and single-walled nanotubes. MWNTs contain overlapping cylindrical tubes, like coaxial cables. Their diameters range from a few nanometers to around 40 nm. The SWNTs consist of graphene cylindrical walls with diameters ranging from 1 and 2 nm and length of few microns. MWNTs have thicker walls, consisting of several coaxial graphene cylinders separated by spacing around 0.34 nm that is close to the interlayer distance in graphite. The outer diameters of MWNTs range between 2 and 40 nm and the inner hollows between ~1 to 8 nm. The aspect ratio of nanotubes varies with the diameter. The average length of the CNTs can vary from several nanometers to few micrometers. Individual SWNTs have uniform diameters, although when formed they also show a strong tendency to pack together in larger bundles. Nanotubes prepared experimentally are observed to be closed at both ends. This involves the introduction of pentagonal topological defects, a minimum of six, on each end of each cylinder in tube.

Thus, the tubes are essentially made of cylinders attached to halves of large fullerene like structures at the ends.

2.3 Production and Synthesis of Carbon nanotubes

Various techniques are being developed for the synthesis of carbon nanotubes. Some of the basic methods used are the carbon-arc discharge method, the laser ablation method, the chemical vapor deposition (CVD) method, the flame synthesis, and Smalley's high-pressure carbon monoxide (HIP-CO) process. To produce CNTs of desired characteristics in large quantities is still a challenging task for the scientists and engineers. It was the arc discharge method through which the first CNTs were synthesized and discovered by Iijima. Single walled carbon nanotubes (SWNTs) are obtained by using a graphite rod containing catalysts like Fe,Co as anode with a pure graphite cathode [9].

In 1991, Iijima reported the synthesis of CNT by means of a carbon-arc discharge evaporation technique. The CNTs are grown at the negative end of the electrode which is used for the arc discharge. CNTs ranging from 4 to 30 nm in diameter and up to 1 μm in length were grown on the negative end of the carbon electrode. Ishigami *et al.* [10] developed a simple arc-method to synthesize CNTs in the liquid nitrogen which allowed the continuous synthesis of high quality multi-walled carbon nanotubes. Large scale synthesis of MWNTs through the arc discharge method using He gas has been achieved by Ajayan *et al* [11].

In the laser ablation method, a pulsed laser is used to vaporize the target graphite at high temperatures in the presence of inert gas. The nanotubes are formed on the surface of the reactor which is relatively cooler. This method gives control on the production of CNT tubes and the process is expensive. Changxin Chen *et al.* [12] have reported large-scale synthesis of carbon nanotubes (CNTs) under normal temperature and pressure, using pulsed laser ablation of a graphite target in metal nano-sol. The metal nano-sol is prepared by laser ablation of metal target in ethanol and used as catalyst. The growth of carbon nanotubes (CNTs) on substrate using a high vacuum laser ablation system was achieved by Takahashi, Syunji *et al.* [13]. CNTs were grown selectively on the carbon particle, such as droplets and graphite powders dispersed on a Si (100) substrate. The CNTs grown on the carbon particles were revealed to be multi-wall carbon nanotubes (MWNTs) having several layers and 15-20° of tip angle. Laser ablation of Ni or Fe is used by Vander Wal, R.L. *et al.* [14] to create nanoparticles within a reactive flame environment for catalysis of carbon nanotubes (CNTs).

Catalytic chemical vapor deposition (CCVD) methods have a great potential for low-cost, large-scale production synthesis of carbon nanotubes. In this process CNTs can be grown on a desired substrate. These methods involve the catalytic decomposition of a carbonaceous gas (hydrocarbon or carbon monoxide) on transition-metal particles. Iron and cobalt have both been found to be effective for the production of SWNTs and DWNTs**.** In MPECVD, Si nanorods are grown on the Si substrate covered with a PtPd thin film of 2 nm thickness and a Fe thin film of 1 nm thickness is deposited on the nanorods as second growth step Vertically aligned carbon nanotubes (CNTs) on the Ni coated TiN/metal substrates were synthesized by Kim, Hyun Suk *et al.* [15] with a plasma-enhanced chemical vapor deposition at 650°C using a gas mixture of NH_3 and

C_2H_2. The diameters of the CNTs were about 80 nm for the stainless steel (SUS304) and 160 nm for the Kovar substrate.

Uniform and well-aligned carbon nanotubes (CNTs) have been grown by Yen, J.H. *et al*. [16] using a high density inductively coupled plasma chemical vapor deposition (ICP-CVD) system. A gas mixture of methane-hydrogen was used as the source and Ni as the catalyst for the CNT growth. The effect of process parameters, such as inductive RF power, DC bias voltage and CH_4/H_2 ratio, on the growth characteristics of CNTs was investigated. It was found that both plasma intensity and ion flux to the substrate, as controlled by the inductive RF power and DC bias voltage, respectively, can greatly affect the growth of CNTs.

The main advantages of CVD techniques are obtaining selective growth on desired substrates, obtaining vertical alignment of the CNTs, control over the diameter of the CNTs and the uniformity of the CNT growth. It is hard to grow aligned CNTs (SWNTs, DWNTs, or MWNTs) by the arc discharge method. Since the growth temperature of the arc-discharge method is higher than that of other CNT synthesis methods, the crystallinity and perfection of the arc-produced CNTs are generally high with high yield per unit time. There are both advantages and disadvantages of using one method over the other hence, a decision of using a particular method for the synthesis must be made based on the required characteristic properties of the CNTs.

2.4 Thermal and Mechanical properties of CNT composites

Because of the high aspect ratio of the CNTs, the conductivity of the polymer composites can be enhanced with even a very low percentile of CNTs added to the matrix material. Significant enhancement of electrical properties is also obtained in nanocomposites based on intrinsically conducting polymers. The CNTs make conjugated polymers mechanically stronger, more conductive and less susceptible to thermal degradation. Composite materials based on CNTs in poly (p-phenylenevinylene-co-2,5-dioctyloxy-m-phenylenevinylene) PmPV exhibited nearly an eightfold increase in electrical conductivity compared to the neat polymer, without impairing the photo- and electro-luminescence properties of the polymer [17]. CNT/epoxy composites show increases in thermal conductivity, K, of 10%_120% when 1% of SWNTs are incorporated [17]. The coefficient of thermal expansion in the longitudinal direction of flow (CTE) is significantly reduced when the nanocomposites is injection molded. CTE reduction enables reduced cure shrinkage and hygrothermal instability in these systems, resulting in better dimensional stability of the material. Thermal stability may be affected by the presence of the nanotubes, which interfere with the mobility and crystallization of the polymer chains, and enable the composite to be used for high temperature applications [17]. The nanotube also helps to delay the onset of thermal degradation of the polymer.

The strength of composites depends on various factors. Load transfer between the matrix and the nanotubes influences the overall strength of the composite. Recent research on bonding between the nanotubes and the surrounding has shown that the use of nanotubes, which are aligned perpendicularly to the cracks are able to slow down crack propagation processes by bridging up the crack faces [18]. The nanotubes should be well dispersed in the matrix material. Poorly dispersed nanotubes will fail by separation rather than by failure of the nanotubes resulting in significantly reduced strength. The strength properties of polypropylene fibers were enhanced with single-wall carbon nanotubes (SWNTs). For a 1-wt % loading of nanotubes, the fiber tensile strength is reported to have increased by 40%.while the modulus increased by 55%.

2.5 Synthesis of CNT Composites

Several processing methods available for producing polymer/CNT composites based on either thermoplastics or thermosets have been mentioned by Breuer, O. *et al.* [17] in their paper "Big returns from small fibers: A review of polymer/carbon nanotube composites." Factors that affect the composite properties are CNT dispersion, alignment, interfacial bonding and deagglomeration of bundles and ropes. The effective utilization of carbon nanotubes in nanocomposites depends strongly on the ability to disperse the CNTs individually and uniformly throughout the matrix. Good interfacial bonding is required to achieve load transfer across the CNT-matrix interface. Despite their intrinsic rigidity and high anisotropy, most currently available forms of CNTs are isotropic and fragile and contain several species. To prepare the material for processing on a macroscopic scale, preprocessing is required. Most production processes generate a range of carbonaceous particles such as amorphous carbon, fullerenes, and nanocrystalline graphite's, and the final effluent includes transition metal catalysts. The most common methods to remove unwanted byproducts are thermal annealing in air or oxygen for selective etching of amorphous carbons, and acid treatment for eliminating catalyst residues. As mentioned earlier nanotubes tend to form bundles in the matrix material which in turn weakens the strength of the nanocomposites. To achieve uniform dispersions of nanotubes in the matrix material deagglomeration is used. The most common method used for deagglomeration is ultrasonicating a CNT solution. Electrostatic plasma treatment is also used to separate CNTs from the larger agglomerated particle mixture of other CNTs and impurities. Electric field manipulation and polymer wrapping have also been proposed to overcome entangling of nanotubes, which results from their strong van der Wals attractions. Chemical functionalization is being used for improving nanotube/matrix interactions in achieving processability and property enhancement. The surface modification will allow the unique properties of CNTs to be coupled with those of other materials in the final product. Several approaches to functionalization have been developed, including defect functionalization; covalent functionalization of the sidewalls; and noncovalent exohedral functionalization with polymers

Various methods have been developed by research groups in synthesis and fabrication of CNT based composite materials. Linear polyethyleneimine (PEI) is ingeniously used as both a functionalizing agent for the multiwalled carbon nanotubes (MWNTs) and a reducing agent for the formation of Au NPs. This method involves a simple mixing process followed by a mild heating process. This approach does not need the exhaustive surface oxidation process of CNTs. A phosphorus nickel-carbon nanotube (Ni-P-CNT) nanocomposites film is synthesized by Shen, Guang-Ren *et al.*[19] for microelectromechanical systems device fabrication. With a special acid oxidative method, a well-dispersed nickel-CNTs colloidal solution has been produced without any aggregation, which is suitable for microstructure fabrication. The nanoindentation measurement indicates that the Young's modulus and hardness of the Ni-P-CNT nanocomposite film plated in the bath with 0.028-g/L CNTs can greatly increase up to 665.9 and 28.9 GPa. Carbon nanotube/poly (p-phenylene benzobisoxazole) (CNT/PBO) composite fibers were prepared by in situ polymerization and dry-jet wet spinning by Li, Jinhuan [20]. Compared with PBO fibers containing no CNTs prepared under the same conditions, the thermal resistance of the CNT (2 wt%)/PBO fibers was reported to be higher along with the increase in tensile strength by 20-50%. CNTs/Fe/Al_2O_3 nanocomposites were prepared by Yoo, S.-H. *et al.* [21] using the thermal CVD and SPS methods. The dispersion of CNTs in the Fe/Al_2O_3 matrix was controlled by an attrition milling process. Through FESEM analysis, it has been reported that the CNTs of 5% volume fraction were homogeneously dispersed in the Fe/Al_2O_3. Fracture strength and electrical conductivity of 5% volume fraction CNTs/Fe/Am_2O_3specimen were reported to be at 641 MPa and 2.93×10^{-11} mS/m, where as that of a 20 vol.% CNTs/Fe/Al_2O_3 specimen were 208 MPa and 8.46×10^{-7} mS/m, respectively. In comparison with an Al_2O_3 monolith, the specimen with 5% volume fraction CNTs has showed enhanced fracture strength and increased electrical conductivity.

CHAPTER 3

FINITE ELEMENT MODELING OF CNT COMPOSITES

3.1 Introduction

This chapter will deal with finite element modeling of CNT-based composites using continuum mechanics. Considerable amount of research is yet to be done in dealing with analytical and experimental methods to address these multiscale, multiphysics problems in the field of nanocomposites particularly fiber reinforced nanocomposites. A finite element model is developed using Representative volume element method. The effective thermal conductivity in axial direction is calculated and compared with the theoretical values obtained from earlier work done using effective medium theory. The FEA analysis also examines the lesser than expected thermal conductivity of the CNT based composites

3.2 Mathematical model for effective conductivity of a CNT nanocomposite

A mathematical solution was developed for the effective conductivity in axial direction by using effective medium theory. Study of heat conduction in a heterogeneous material like CNT based nanocomposite was done using this theory. According to the effective medium theory a heterogeneous material having discontinuous properties can be replaced in an equivalent sense, by a homogeneous material that gives the same average response to a given input at the macroscopic level. This process is called homogenization. The volume averaging method of homogenization with dilute assumption was considered for this particular case and the composite is assumed to be statistically homogeneous. In statistically homogeneous composite the fillers are uniformly dispersed within the matrix material. This assumption simplifies the mathematical analysis to a greater extent. The steady state heat conduction with no heat generation was considered for developing a mathematical model.

The development of a continuum model for an MWNT inclusion was done in two distinct steps. First, an equivalent continuum model of an MWNT was developed by taking into account the mechanism of heat conduction through an MWNT. Once this is done, the structure and properties of the nanotube are taken into account and the properties of an effective fiber are defined. This effective fiber is then considered to be the inclusion phase that is embedded within the matrix material. The composite material to be analyzed is effectively an aligned short fiber composite, where the effective fiber constitutes phase that is embedded within a polymer matrix. A mathematical solution for calculating thermal conductivity of a CNT composite in the longitudinal direction using effective medium theory was developed by Bagachi and Nomura [22].

3.3 Equivalent continuum model and effective solid fiber

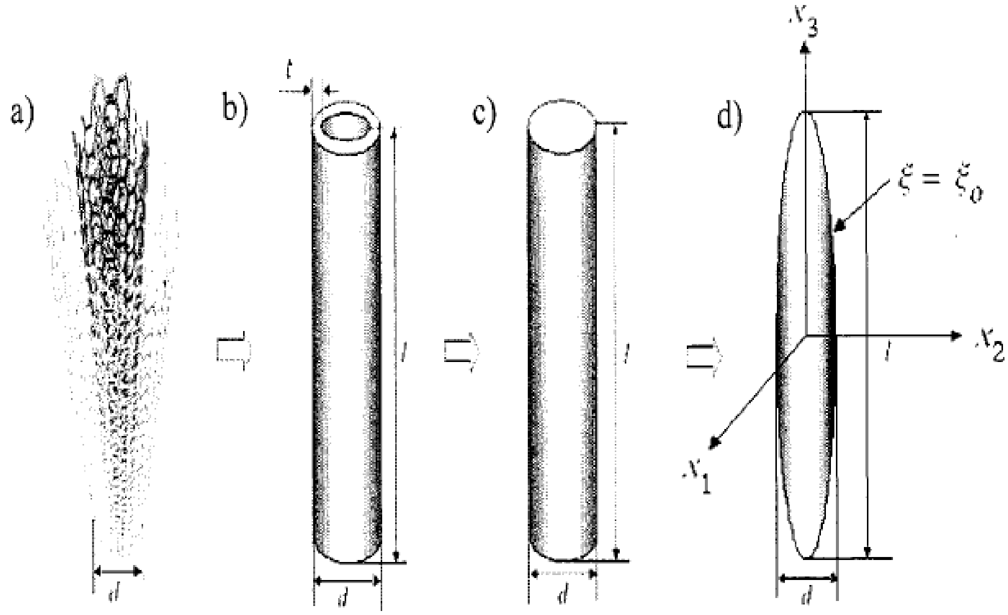

Figure 3.1: Development of a continuum model for an MWNT. a) Schematic diagram of an MWNT showing concentric graphene layers. b) Equivalent continuum model; c) Effective solid fiber, and d) a prolate spheroidal inclusion. [22]

In developing a continuum model for an MWNT consideration has to be given to the contribution of the individual nanotube layers to the thermal transport through nanotube. The contribution of individual layers in thermal transport of CNT has not been studied in detail. Kim et al.[23] have suggested that since only outer nanotube layer makes good thermal contact with the surrounding medium, the contribution to thermal transport through the nanotube will be higher than the inner layers. It is assumed that only outer MWNT layer is involved in the conduction of heat through the nanotube since the contribution of individual layers is unknown and in the present study. Since only outer layer is in thermal contact with the surrounding matrix material they are thus responsible for the exchange of heat between the nanotube and the matrix. A hollow cylinder having the same length and diameter as that of the nanotube is considered to represent an equivalent continuum model of the nanotube. The thickness of the cylinder wall is the same as that of outer nanotube layer (0.34nm) and considered it to be made up of a homogeneous and isotropic material that has the same physical properties as that of the nanotube. The heat carrying capacity of this hollow cylinder is applied to its entire cross section and the properties of an effective solid fiber are defined [22].

Effective fiber can be defined as a solid fiber that has the same length and diameter as that of the hallow cylinder and has an identical temperature gradient across its length when the same amount of heat is flowing through it. This effective fiber thus retains the geometrical properties of the nanotube while providing us with a continuum model of the nanotube structure that is suitable for mathematical analysis.

The expression for the conductivity of the effective solid fiber in the longitudinal direction is given by following equation [22]

$$k^{(2)} = \frac{4t}{d} k_{NT} \qquad (t/d < 0.25) \tag{3.1}$$

Where d represents nanotube diameter, t represents the thickness of the outer wall of the nanotube. Very little study has been made on the theoretically and experimentally on the conductivity of the nanotube in the transverse directions. For simplicity, we consider the thermal conductivity of the effective fiber to be isotropic in nature. The expression for the effective thermal conductivity of a CNT composite having isotropic cylindrical short fibers as the filler material where the conductivity of the filler material is given by equation [22] and has a contact resistance at the interface is.

$$k_{33}^{*} = k^{(1)}\left[1+v_2\left(1+\lambda B_1\right)f\left(\xi_o\right)\right] \tag{3.2}$$

Where v2 is the volume fraction of the nanotube phase and λ are defined as

$$f\left(\xi_o\right) = \left[\frac{1}{2}\xi_o\left(\xi_o^2-1\right)\ln\left(\frac{\xi_o+1}{\xi_o-1}\right)-\xi_o^2\right]^{-1} \tag{3.3}$$

$$\lambda = \frac{k^{(2)}}{k^{(1)}} \tag{3.4}$$

The quantity ξ_o is the inverse of the eccentricity of the spheroid and is given by

$$\xi_o = \left(1-\frac{a_1^2}{a_3^2}\right)^{-\frac{1}{2}} \tag{3.5}$$

$$c = \left(a_3^2-a_1^2\right)^{\frac{1}{2}} \tag{3.6}$$

The constant ***B1*** can be obtained as a solution to the following linear simultaneous equations.

$$\delta(n)+B_{2n+1}\left[1-(1-\lambda)\left(\xi_o^2-1\right)\dot{P}_{2n+1}\left(\xi_o\right)Q_{2n+1}\left(\xi_o\right)\right] = \left(\frac{\lambda}{\overline{\beta}}\right)\sum_{m=0}^{\infty}B_{2\dot{m}+1}\chi_{nm}\left(\xi_o\right) \tag{3.7}$$

Where the coefficients interfacial conductance β and $\chi_{nm}\left(\xi_o\right)$ are given by

$$\chi_{nm}\left(\xi_o\right) = \left(\frac{4n+3}{2}\right)\left(\xi_o^2-1\right)\dot{Q}_{2n+1}\left(\xi_o\right)\dot{P}_{2m+1}\left(\xi_o\right)\int_{-1}^{1}\left(\frac{\xi_o^2-1}{\xi_o^2-\mu^2}\right)^{\frac{1}{2}}P_{2n+1}(\mu)P_{2m+1}(\mu)\,d\mu \tag{3.3}$$

$$\overline{\beta} = \frac{\beta c}{k^{(1)}} \tag{3.8}$$

P_n, Q_n Are know as Legendre polynomials of first kind and second kind respectively and

$$P_n(z) = \frac{1}{2^n n!}\frac{d}{dz^n}\left(z^2 - 1\right)^n, \tag{3.9}$$

$$Q_n(z) = \frac{1}{2}P_n(z)\ln\frac{z+1}{z-1} - W_{n-1}, \tag{3.10}$$

where

$$W_{n-1}(z) = \frac{1}{2}P_0(z)P_{n-1}(z) + \frac{1}{n-1}P_1(z)P_{n-2}(z) + \dots\dots + P_{n-1}(z)P_0(z), \tag{3.11}$$

$\delta(n)$ is defined as

$$\delta(n) = \begin{cases} 1 & if\ n = 0 \\ 0 & otherwise \end{cases} \tag{3.12}$$

3.4 Finite element modeling of a CNT Representative Volume Element (RVE)

Study of computational modeling and simulation of the nanocomposites can play a significant role in the development of superior nanocomposites. Modeling and simulations will help in understanding the behavior of nano structures under various loads and environments. At the nanoscale, analytical models are difficult to establish, while experiments are expensive to conduct. A detailed study on the material characterization of various nanocomposites is yet to be done. It is very important to know how material properties of nanocomposites such as thermal and electrical conductivity, yield strength, thermal expansion, etc are influenced by factors like synthesis procedure, external load, wear, friction, shock, moisture, electric and magnetic fields etc.

Finite element modeling of composite materials at the nanoscale using continuum mechanics approach is a challenging task. The assumptions made while modeling a fiber reinforced composite in macro scale may or may not hold good depending on the nature of analysis that is being carried out.

There is always a concern for using finite element methods which are based on the principles of continuum mechanics in modeling a nanoscale problem where the load and heat transfer occurs at the atomic level. If the objective of the simulation is to study the local interactions among individual atoms and the chemical reactions between the CNT and a matrix material, then the mathematical models based on quantum mechanics or molecular dynamics (MD) should be adopted. However, if the purpose of the simulation is to investigate the global responses of individual CNTs or CNT-based composites, such as deformations, load and heat transfer mechanisms, and effective stiffness of the nanocomposites, then the continuum mechanics approach may still be applied safely to study the problem effectively and efficiently [24]. The geometric parameters of the nanotube make the task more difficult. CNTs behave as a shell in the matrix where the shell thickness is approximately 0.34nm. This is very difficult to model for various reasons like computational recourses, difficulty in meshing large amount of CNTs, and compatibility of shell elements with the solid elements. Since shell and solid elements have different degree of freedoms they are not compatible with each other. It is difficult to couple shell models with the 3-D solid model used for the matrix at the interfaces. The solid and shell models involve different types of variables and degrees of freedom. It is wise to use 3-D elements for meshing both matrix and the

CNT. For the analysis of CNTs embedded in matrix material, Solid models of the CNTs will provide better accuracy among all the continuum mechanics models.

Carbon nanotube composites are made up of CNTs with different sizes and forms dispersed in a matrix. They can be single-walled or multi-walled with varying geometric parameters like length, diameter, and straight, twisted, curled etc. The CNTs can be oriented in a particular direction and orientation in the matrix or it can be dispersed randomly. All these factors make the simulations of the mechanical nanotube-based materials extremely complicated. The concept of unit cells or representative volume elements have been applied successfully in the studies of conventional fiber-reinforced composites at the microscale level and many researchers have extended this to the study of CNT-based composites at the nanoscale. In RVE approach, a single nanotube with surrounding matrix material is modeled, with properly applied boundary and interface conditions to account for the effects of the surrounding materials it is possible to study the nanocomposite based on the single Representative volume element. This RVE model can be employed to study the interactions of the nanotube with the matrix. It is possible to model and evaluate the effective material properties of the nanocomposite.

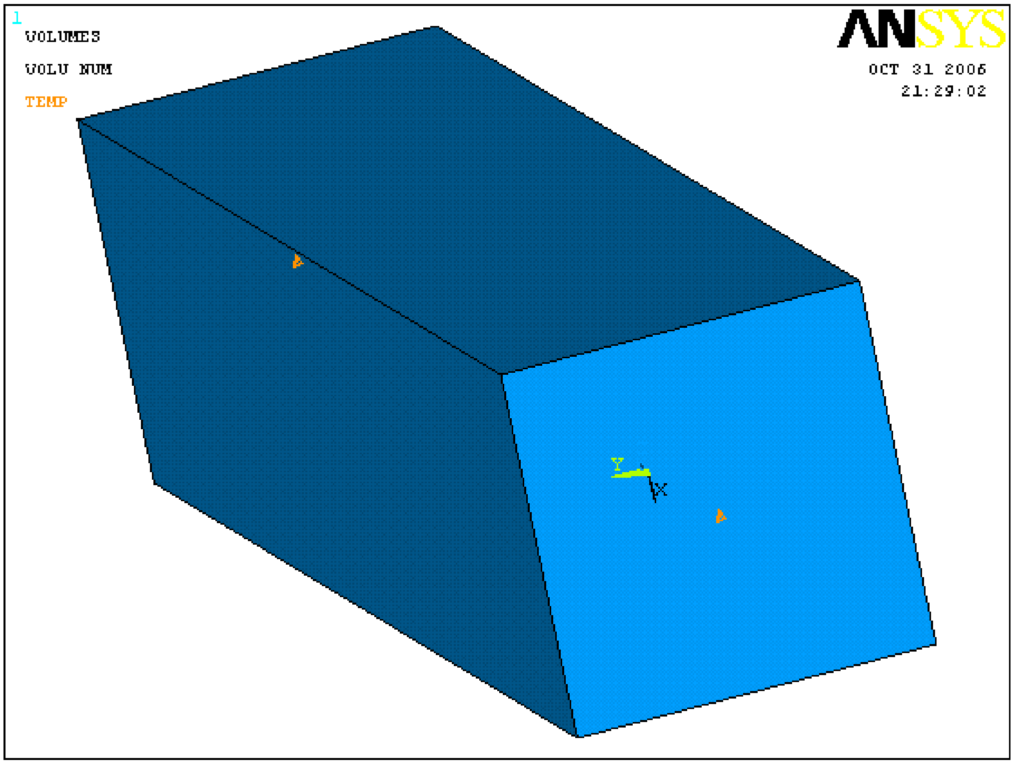

Figure 3.2: Representative volume element (RVE) with a single equivalent solid MWNT fiber composite inclusion.

Different types of representative volume elements are used in modeling a fiber reinforced composite material. They can be classified according to the shape of the cross section, circular RVE, rectangular or square RVE and hexagonal RVE. The square RVE models can be applied when the CNT fibers are arranged evenly in a square pattern, while the hexagonal RVE models can be applied when CNT fibers are in a hexagonal pattern, in the transverse directions [24].

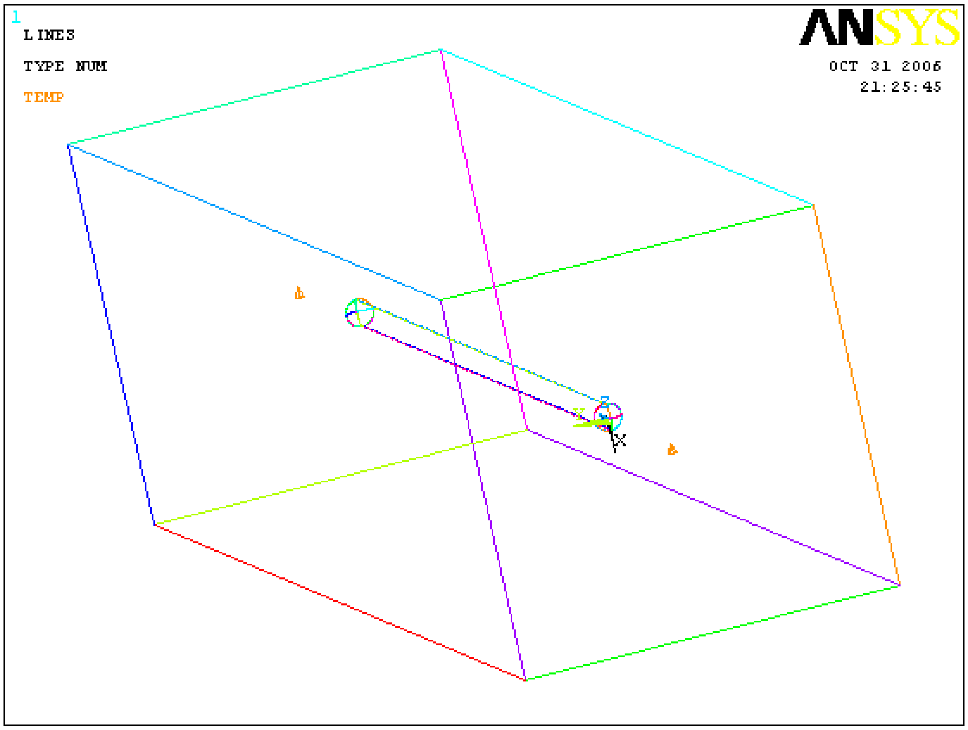

Figure 3.3: Representative volume element (RVE) with a single equivalent solid MWNT fiber composite inclusion. (Wire frame model)

Interfaces between the carbon nanotubes and matrix are crucial regions for the functionality and reliability of CNT-based nanocomposites. The heat carrying capacity of a CNT based nanocomposite depends on how good the heat is transferred from the matrix material to the carbon nanotube. Since all the heat must be transferred through the interfaces to CNTs a good thermal contact between the matrix and the carbon nanotube becomes very essential. Most failures of mechanical failures in CNT based nanocomposites occur at or around the interfaces. The interface debonding, friction/wear, instability, or matrix cracking etc may occur due to difference in the stiffness and other physical or chemical properties. Modeling thermal interfaces is always a serious challenge to any simulation technique based on the continuum mechanics and it becomes more difficult in microscopic level and the models which are in the nanoscale. Thus, simulations results near the interfaces should be interpreted carefully.

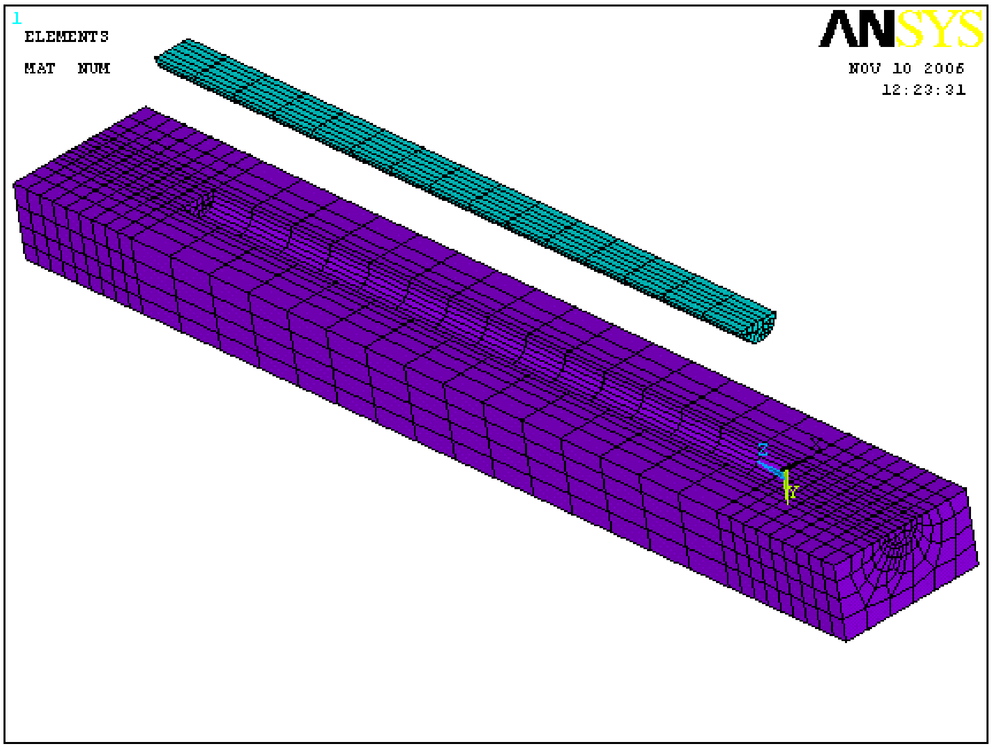

Figure 3.4: Meshed representative volume element with single effective solid fiber inclusion (half model) for illustration.

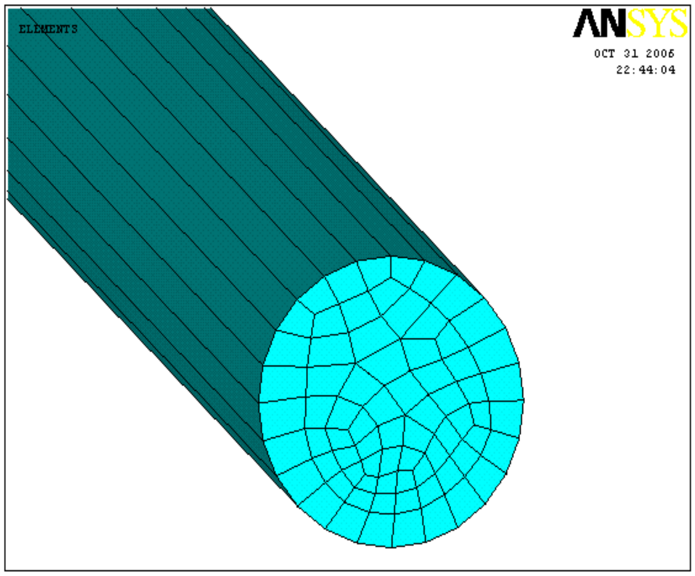

Figure 3.5: Effective fiber meshed with solid elements

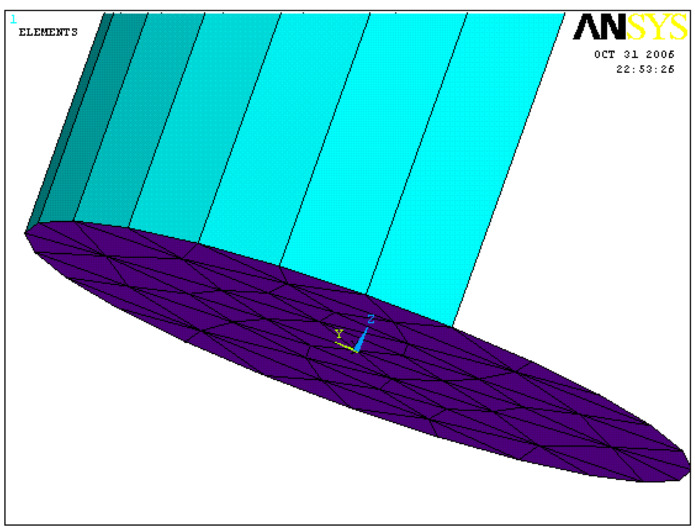

Figure 3.6: Effective fiber meshed with contact and target surface elements. (Partial view for illustration)

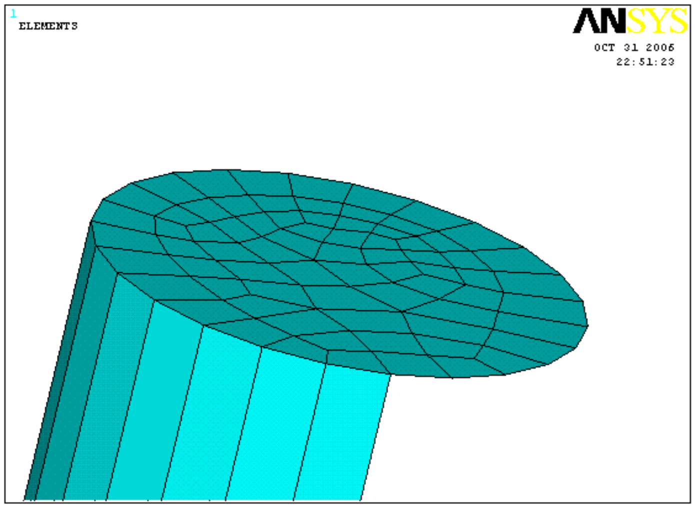

Figure 3.7: Effective fiber meshed with contact surface elements. (Partial view for illustration)

3.5 Determining effective conductivity from the finite element analysis results

Thermal conductivity of the composite is calculated using Fourier’s law. According to Fourier's law, Thermal conductivity is the ability of the material to transfer heat from a region of high temperature to a region of low temperature and is given by the relation

$$q = -kA\frac{dT}{dx} \tag{3.13}$$

where q is the heat flow, k is the thermal conductivity, A is the cross sectional area and dT/dx is the temperature gradiant in the direction of flow.

Using proper tools in the analysis package thermal heat flux and thermal gradient at each node of the meshed volume (RVE) is collected. The volume average of heat flux and the thermal gradient is calculated. Effective thermal conductivity of the

Representative volume element is determined by the ratio of volume average heat flux to the volume average of temperature gradient

i.e.

$$k_{eff} = \frac{volume \quad average \quad of \quad heatflux}{volume \quad average \quad of \quad thermal \quad gradient} \tag{3.14}$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

In this chapter, the data obtained from the finite element analysis of representative volume element composite material is presented. The analysis is carried out varying different parameters such as diameter, length, volume fraction of the CNT in a composite and the interface resistance between the matrix and the CNTs. The effective thermal conductivity of the RVE is calculated using the procedure discussed in the previous chapter. Obtained data are analyzed and interpreted comparing with the theoretical values. Different parameters that are influencing the overall thermal conductivity of the composite are discussed in order to have a better understanding of heat transport mechanism in CNT based nanocomposite materials. The result analysis shows various factors that may be responsible for the lower than expected thermal conductivity.

4.2 Numerical Calculations

Table 4.1: Geometric and material properties of MWNT and the polymer matrix material considered in the finite element analysis.

Sl. no	Description	Symbol	Units	Value
1	Average nanotube diameter	d	Nm	25
2	Average nanotube length	l	µm	30
3	Conductivity of polymer matrix	$k^{(1)}$	W/m-K	0.20
4	Conductivity of MWNT	k_{NT}	W/m-K	3000
5	Interfacial conductance	β	MW/m^2 K	12
6	Conductivity of effective fiber	$k^{(2)}$	W/m-K	-
7	Thickness of the outer nanotube layer	t	Nm	0.34

Numerical calculation is carried out to determine the effective thermal conductivity in the axial direction of an aligned MWNT polymer composite. The software program, Mathematica, has been used to solve the linear differential equations and to calculate various constants involved in the equation (3.2) for the thermal conductivity [22]. The effective thermal conductivity is calculated by varying the length of the CNTs keeping the diameter as constant *i.e.* varying the aspect ratio with a fixed diameter and values of nodal heat flux and the temperature gradient is tabulated. The same procedure is carried out varying the diameter of the CNTs from 20 nm to 45 nm keeping the length of the CNTs to be constant. For a fixed aspect ratio, the interface conductance is varied and the theoretical behavior is studied. Dependence of the thermal conductivity on the volume fraction is studied by keeping the aspect ratio constant and varying the volume fraction of the CNT in the composite.

The following mathematical formulas developed by Bagchi and Nomura [22] are used in calculating the effective thermal conductivity in the axial direction of the CNT *i.e.* in the x_3 direction.

$$k_{33}^{*} = k^{(1)}\left[1 + v_2\left(1 + \lambda B_1\right) f\left(\xi_o\right)\right] \tag{4.1}$$

Where v_2 is the volume fraction of the nanotube phase and λ is defined as

$$f\left(\xi_o\right) = \left[\frac{1}{2}\xi_o\left(\xi_o^2 - 1\right)\ln\left(\frac{\xi_o + 1}{\xi_o - 1}\right) - \xi_o^2\right]^{-1} \tag{4.2}$$

$$\lambda = \frac{k^{(2)}}{k^{(1)}} \tag{4.3}$$

The conductivity of effective solid fiber of MWNT is given by

$$k^{(2)} = \frac{4t}{d} k_{NT} \tag{4.4}$$

The constant ***B1*** can be obtained as a solution to the following linear simultaneous equations:

$$\delta(n) + B_{2n+1}\left[1 - (1-\lambda)\left(\xi_o^2 - 1\right)\dot{P}_{2n+1}\left(\xi_o\right) Q_{2n+1}\left(\xi_o\right)\right] = \left(\frac{\lambda}{\overline{\beta}}\right)\sum_{m=0}^{\infty} B_{2m+1}\chi_{nm}\left(\xi_o\right) \tag{4.5}$$

Where the coefficient interfacial conductance, β and $\chi_{nm}\left(\xi_o\right)$, are given by

$$\chi_{nm}\left(\xi_o\right) = \left(\frac{4n+3}{2}\right)\left(\xi_o^2 - 1\right)\dot{Q}_{2n+1}\left(\xi_o\right)\dot{P}_{2m+1}\left(\xi_o\right)\int_{-1}^{1}\left(\frac{\xi_o^2 - 1}{\xi_o^2 - \mu^2}\right)^{\frac{1}{2}} P_{2n+1}(\mu) P_{2m+1}(\mu)\, d\mu \tag{4.6}$$

$$\overline{\beta} = \frac{\beta c}{k^{(1)}} \tag{4.7}$$

Where P_n, Q_n are known as the Legendre polynomials of first kind and second kind, respectively, and were introduced in the previous chapter.

Numerical calculation for a nanocomposite with the CNT diameter of 25 nm and length of 30 μm is illustrated below.

We can now calculate ξ_o and c using equations (3.5) and (3.6) defined in the previous chapter.

We get

$$\xi_o = \left(1 - \frac{a_1^2}{a_3^2}\right)^{-\frac{1}{2}} \tag{4.8}$$

$$\xi_o = \left(1 - \frac{d^2}{l^2}\right)^{-\frac{1}{2}} = 1.000000374 \tag{4.9}$$

$$c = \left(a_3^2 - a_1^2\right)^{\frac{1}{2}} \tag{4.10}$$

$$c = \left[\left(\frac{l}{2}\right)^2 - \left(\frac{d}{2}\right)^2\right] \tag{4.11}$$

$$=14999.9948\text{nm}. \tag{4.12}$$

The quantity, $f(\xi_o)$ is calculated using equation (4.2) as

$$f(\xi_o) = \left[\frac{1}{2}\xi_o\left(\xi_o^2 - 1\right)\ln\left(\frac{\xi_o + 1}{\xi_o - 1}\right) - \xi_o^2\right]^{-1}$$

$$=-1.000004711 \tag{4.13}$$

The conductivity of the effective fiber is given by equation (4.4) as

$$k^{(2)} = \frac{4t}{d}k_{NT}$$

$$=163.2\text{W/mK}, \tag{4.14}$$

Now the values of λ and $\overline{\beta}$ are calculated using the following relation given by equations (4.3) and (4.7)

$$\lambda = \frac{k^{(2)}}{k^{(1)}}$$

$$=816 \tag{4.15}$$

$$\overline{\beta} = \frac{\beta c}{k^{(1)}}$$

$$=900.00 \tag{4.16}$$

We now solve the equation xx using *Mathematica* to get the constant B_1.

$$B_1 = -0.99441414 \tag{4.17}$$

The effective conductivity can be calculated using equation (4.1) as

$$k_{33}^{*} = k^{(1)}\left[1 + v_2\left(1 + \lambda B_1\right) f\left(\xi_o\right)\right]$$

$$k_{33}^{*} = 1.8248 \text{ W/m-K} \tag{4.18}$$

Similar calculations are done for different cases and are tabulated.

4.3 Finite element analysis

In this section, the analyses conducted varying different parameters are presented. The following assumptions made during the mathematical modeling hold good for the finite element modeling too. A heterogeneous material having discontinuous properties is replaced by a homogeneous material that gives the same average response to a given input at the macroscopic level. This process of homogenization was applied in finding the thermal conductivity of effective solid fiber which replaces an MWNT as the inclusion phase in the representative volume element.

The thermal conductivity of the effective solid fiber is considered in the finite element modeling of RVE. The volume averaging method of homogenization with the dilute assumption was considered where the composite is assumed to be statistically homogeneous *i.e.* the fillers are uniformly dispersed within the matrix material. Interactions between the individual nanotubes are neglected. These two assumptions are very important factors in finite element modeling of a CNT nanocomposite. This assumption allows us to consider the CNT nanocomposite to be made up of a number of unit cells (RVE) in a 3-dimensional space. A single unit cell (RVE) with periodic boundary conditions can be used to do certain FEA analysis of the whole problem. The steady state heat conduction with no heat generation was considered for developing the mathematical model. This assumption allows us to simplify the boundary conditions in the finite element modeling. The two faces of the RVE in the direction perpendicular to the axis of the fiber inclusion are applied with one degree temperature difference. The other four faces of the RVE are applied with adiabatic boundary conditions.

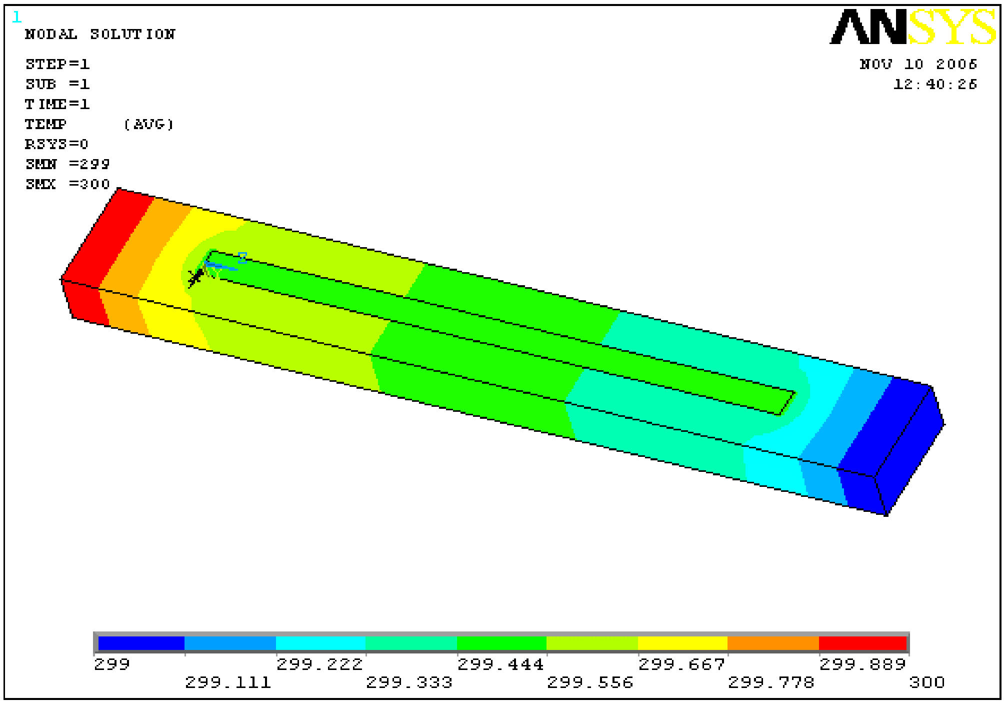

Figure 4.1: Temperature profile in representative volume element (half model).

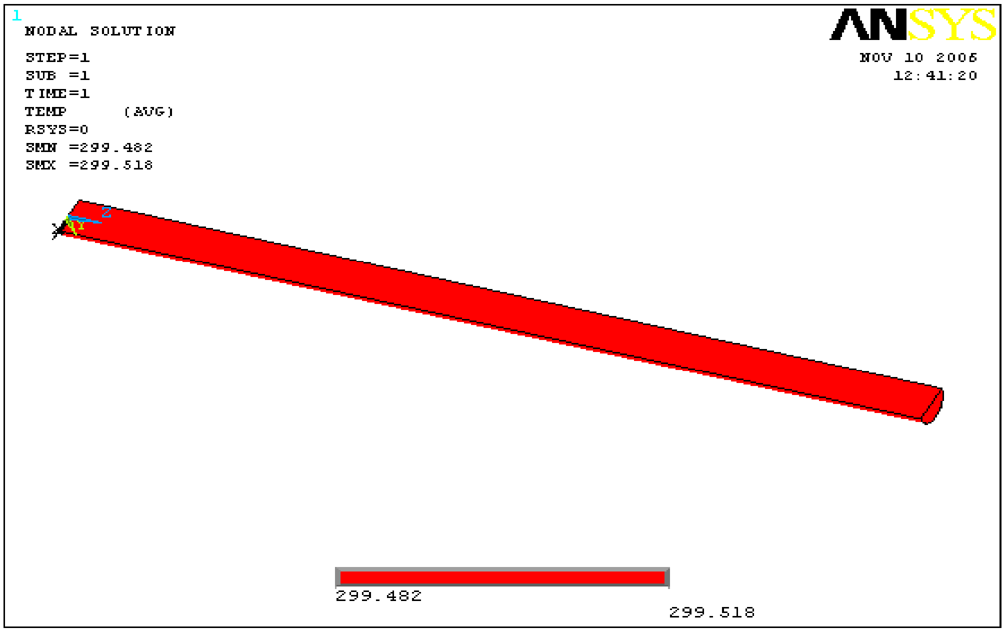

Figure 4.2: Temperature profile in the solid fiber inclusion (half model).

4.3.1 Effect of MWNT length on the effective thermal conductivity of the nanocomposite

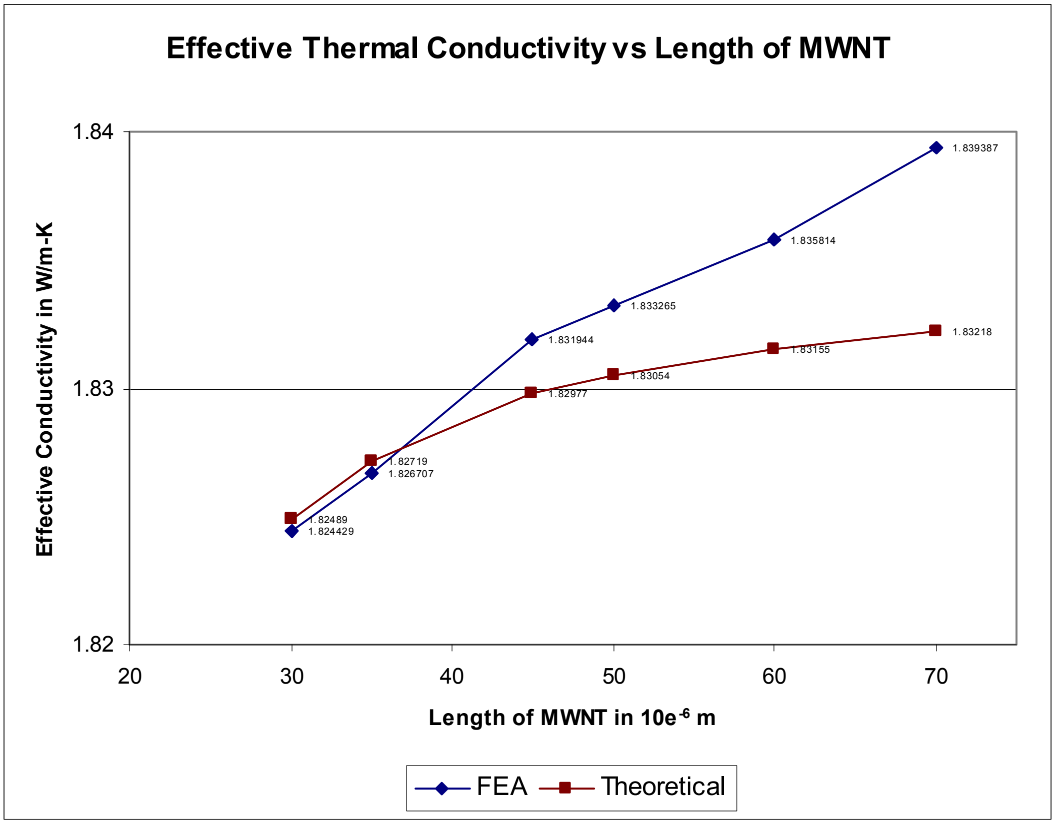

Figure 4.3: Theoretical and FEA results of effective thermal conductivity with varying lengths of MWNT.

Table 4.2: Theoretical and FEA results for effective thermal conductivity of nanocomposites with varying lengths of MWNT.

Sl.No	Length of MWNT (microns)	FEA results W/m-K	Theoretical result W/m-K	Deviation from theoretical results	Percent Deviation (%)
1	30	1.824429	1.82489	0.000461	0.025
2	35	1.826707	1.82719	0.000483	0.026
3	45	1.831944	1.82977	-0.002174	-0.119
4	50	1.833265	1.83054	-0.002725	-0.149
5	60	1.835814	1.83155	-0.004264	-0.233
6	70	1.839387	1.83218	-0.007207	-0.393

This set of analysis was conducted for RVEs with constant MWNT diameters and a fixed volume fraction of 1 %. The objective of the analysis is to study the influence of MWNT fiber length with high aspect ratios. Theoretical calculation has shown that the thermal conductivity increases with increase in length of CNT. However it can be noticed that the effective conductivity does not increase drastically when the length of the MWNT increases from 30 μm to 60 μm. We need to notice that the aspect ratio for an MWNT with 25 nm in diameter and 30 μm in length is around 1,200 and the aspect ratio for the MWNT with the length of 60 μm is around 2,400. In other words, there is no drastic increase in the conductivity for MWNT composites with high aspect ratios. In Figure 4.3, we can notice that the results obtained through FEA analysis is in close agreement with the theoretical results.

4.3.2 Effect of MWNT diameter on the effective thermal conductivity of the nanocomposite

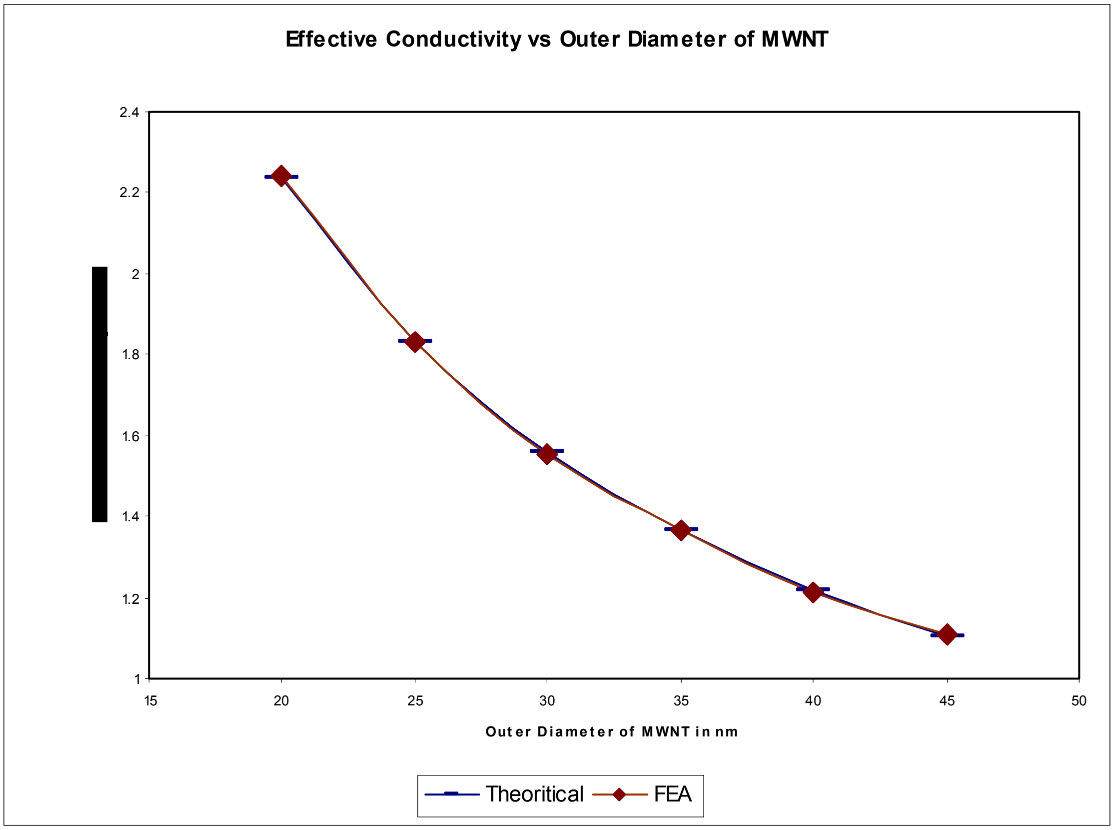

Figure 4.4: Theoretical and FEA results of effective thermal conductivity for varying outer diameter of MWNT keeping length constant.

Table 4.3: Theoretical and FEA results for effective thermal conductivity of nanocomposite with varying outer diameter of MWNT keeping length constant.

Sl.No	Diameter of MWNT (nm)	FEA results W/m-K	Theoretical result W/m-K	Deviation from theoretical results	Percent Deviation (%)
1	20	2.242232	2.2382	-0.004032	-0.180
2	25	1.83066	1.83054	-0.00012	-0.007
3	30	1.55403	1.55878	0.00475	0.305
4	35	1.364191	1.36467	0.000479	0.035
5	40	1.214146	1.21909	0.004944	0.406
6	45	1.110444	1.10587	-0.004574	-0.414

This analysis was conducted to study the effect of MWNT diameter on the effective thermal conductivity of the nanocomposites. The analysis was conducted for 1

% volume fraction of MWNT inclusions where the length of the fiber is kept constant at 50 μm and the diameter is varied from 20 nm to 45 nm. It can be observed from Figure 4.4 that the thermal conductivity is inversely proportional to the diameter of the MWNT inclusions. It is clear that increasing the diameter decreases the effective thermal conductivity.

4.3.3 Effect of thermal contact conductance on the effective thermal conductivity of the nanocomposite

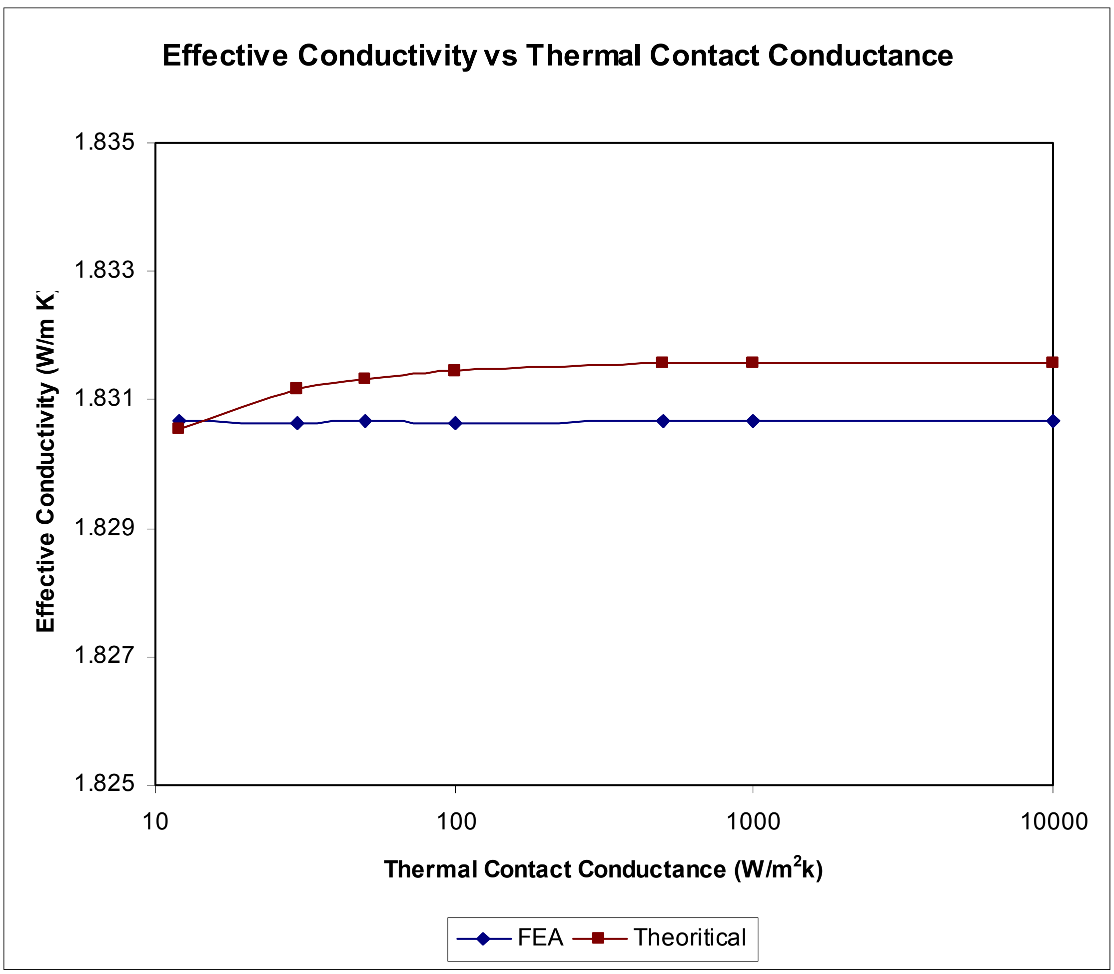

Figure 4.5: Theoretical and FEA results of effective thermal conductivity with varying thermal contact conductance. (Length is 50 μm and diameter of MWNT is 25 nm)

Table 4.4: Theoretical and FEA results for effective thermal conductivity of nanocomposite with varying thermal contact conductance (fixed aspect ratio).

Sl.No	Thermal Contact Conductance (MW/m^2 K)	FEA results (W/m-K)	Theoretical result (W/m-K)	Deviation from theoretical results	Percent Deviation (%)
1	12	1.830664	1.83054	-0.000124	-0.007
2	30	1.83065342	1.831160	0.00050658	0.028
3	50	1.830656	1.83133	0.000674	0.037
4	100	1.830653	1.83146	0.000807	0.044
5	500	1.830669	1.83156	0.000891	0.049
6	1000	1.830674	1.83157	0.000896	0.049
7	10000	1.830676	1.83158	0.000904	0.049

Figure 4.5 shows the relationship between the thermal contact conductances with the effective thermal conductivity. This analysis has been carried out for a 1 % volume fraction MWNT nano composite material with a constant aspect ratio. The thermal contact conductance is varied from 12 Mw/m^2-K to 10,000 MW/m^2K. The objective of the analysis is to study the influence of thermal interface conductance on the effective thermal conductivity of MWNT composite. The effective thermal conductivity is not affected by the increase of thermal contact conductance. The MD simulation conducted by Shenogin [4] has attributed the lower than expected thermal conductivity of the nanocomposite to the interphase resistance. Both theoretical and FEA studies done in this paper show that the thermal conductivity is not greatly affected by the presence of the interphase resistance between the matrix and the CNT inclusions.

4.3.4 Effect of volume fraction on the effective thermal conductivity of the nanocomposite

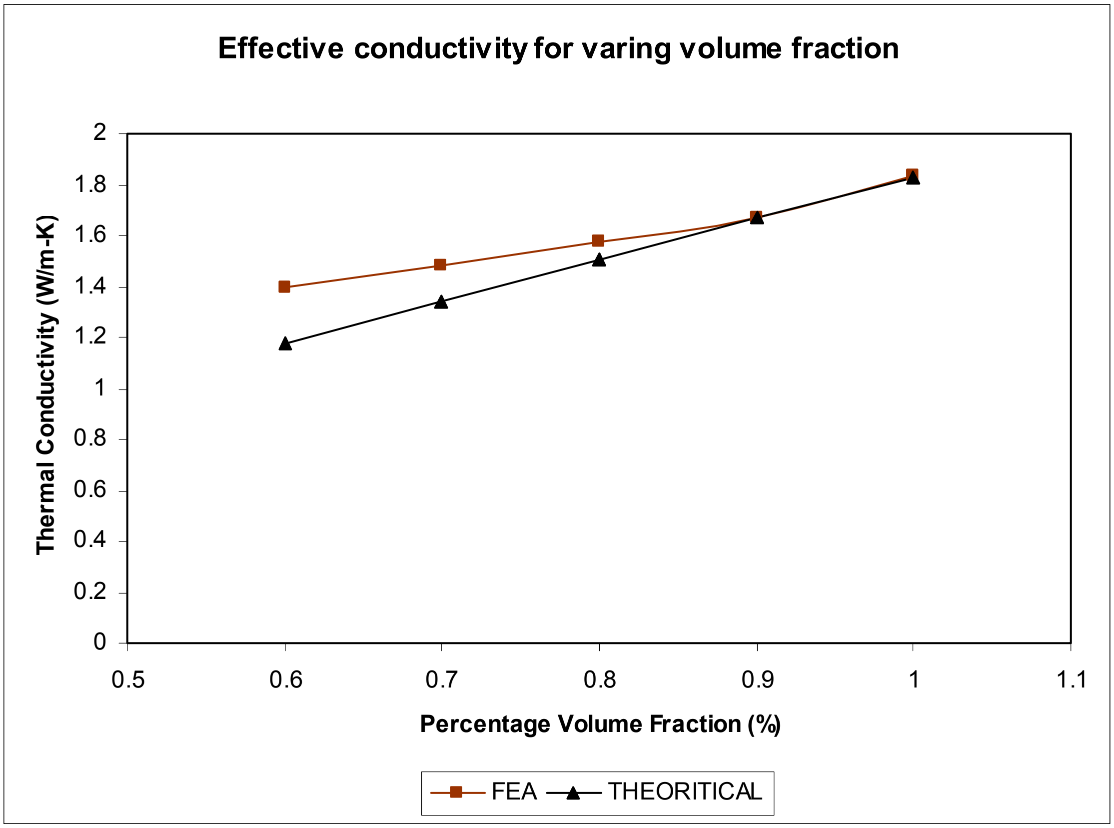

Figure 4.6: Theoretical and FEA results of effective thermal conductivity with varying volume fraction for a fixed aspect ratio (length is 50 μm and diameter of MWNT is 25 nm)

Table 4.5: Theoretical and FEA results of effective thermal conductivity of nanocomposite with varying volume fraction of the composite material.

Sl.No	Volume fraction (%)	FEA results W/m-K	Theoretical result W/m-K	Deviation from theoretical results	Percent Deviation (%)
1	0.6	1.394924	1.178323	-0.2166	-18.3821
2	0.7	1.481002	1.341377	-0.13963	-10.4091
3	0.8	1.574998	1.504431	-0.07057	-4.69061
4	0.9	1.671189	1.667485	-0.0037	-0.22213
5	1	1.833265	1.83054	-0.00272	-0.14886

Figure 4.6 shows the relationship between the volume fraction and the effective thermal conductivity of the composite. We can observe that the thermal conductivity of the nano composite varies linearly with the change in volume fractions as predicted by theoretical model. Since interaction between the nanotubes are neglected both in the theoretical and FEA model of representative volume element the linear behavior is predictable. From the table 4.5 we can notice that even at lower volume fractions the CNT inclusions are able to enhance the thermal conductivity of the matrix material. This is a very important property from the point of thermal management of electronic devices. It is possible to enhance thermal conductivity of the matrix material even with randomly dispersed nanotubes in the matrix material, though the increase may not be as high as in a composite with highly aligned nanotubes but this can help in reducing the production cost of the composite.

From the above studies, it can be seen that there are various factors which may contribute to lowering the effective thermal conductivity predicted by various theoretical models. The theoretical models are based on various assumptions and these assumptions also affect the effective conductivity obtained theoretically, experimentally and through computational methods. The CNT composite is assumed to be statistically homogeneous *i.e.* the fillers are uniformly dispersed within the matrix material. The sample specimen used for experimental calculation may not fulfill these criteria. As discussed in the previous chapters on the properties of CNT composites, CNT's tendency to agglomerate in the composite may influence experimental values. The CNTs in the composite are assumed to be aligned axially, while it is very difficult to obtain a completely aligned CNT composite. It is a well-accepted fact that CNTs aligned randomly tend to lower the effective conductivity. It is also clear from the above analysis that though the interface resistance influences the effective conductivity, it is not the major factor for the less than expected thermal conductivity of the nanocomposites. Very little is known about the thermal properties of the CNTs in transverse directions. The lower than expected thermal conductivity of the CNT based composites in the experimental conditions will also be influenced by the properties in transverse directions. CNTs which are not isotropic in their thermal conductivity and having lower conductivity in transverse directions can reduce the effective conductivity.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORKS

5.1 Conclusions

In this thesis, the effective thermal conductivity of the CNT nanocomposite was studied. A finite element model of the nanocomposite was developed using representative volume element (RVE) method. The interface resistances between the nanotubes and the matrix material were incorporated in the finite element model using thermal contact and target elements. The results obtained were in agreeable range of the theoretical predictions from Bagchi and Nomura [22].

The analysis was carried out with different RVEs which were modeled for studying specific geometric and material properties. The FEA analysis was carried out on the four main influencing factors for the thermal conductivity of the nanocomposites that are length of the nanotube inclusion, diameter of the nanotube inclusion, interface resistance between the nanotubes and the matrix material and volume fraction of the nanotube inclusions in the matrix material. Following are the brief summary and conclusion of individual analysis mentioned above.

1. The analysis on the RVEs with constant diameter and varying lengths revealed that the effective thermal conductivity of a nanocomposite with MWNTS of high aspect ratio increases. How ever the increase in the thermal conductivity with increasing lengths of the MWNTs is not drastic. This also implies that the

2. MWNT inclusions with high aspect ratios can behave as a continuous fiber inclusion in the matrix material.
3. The FEA analysis of RVEs which were modeled with MWNTs having fixed length and varying diameters showed that the effective thermal conductivity of the nanocomposites with volume fractions of 1% decreases with increase in diameter of the MWNT inclusions. Keeping the volume fraction constant was one of the factors for getting the FEA results as predicted theoretically.
4. The FEA analysis on the set of RVEs which has MWNTs with geometric parameters fixed *i.e.* length, diameter and volume fraction of MWNT composite kept constant with different thermal contact resistance showed that the effective thermal conductivity is not greatly affected with change in interface resistance. This is in accordance with the theoretical predictions.
5. The FEA analysis of the RVEs with same MWNT inclusion and varying volume fractions showed that the effective thermal conductivity of the CNT varies linearly. This is as predicted with the theoretical model. One of the reasons for getting liner relationship of effective conductivity with the volume fraction is because of the assumption made during mathematical and FEA modeling of the nanocomposite that there is no interaction between the neighboring MWNT inclusions.

The above studies on the thermal conductivity in nanocomposites suggest that interphase resistances are not the prime factor for getting lower than the predicted thermal conductivities. The uniformity and consistency of certain parameters such as lengths and diameters of the CNT inclusions can greatly affect the overall thermal conductivities. Control over these parameters is vital in obtaining a nanocomposite with desired thermal properties. This study also validates the use of finite element analysis of nanomaterials based on continuum mechanics approach when the object of study is on the overall behaviors of the nanocomposites.

5.2 Recommendations for future works

Various assumptions are made during the mathematical and FEA modeling of CNT nanocomposite to simplify the problem but it has to be noted that these assumed factors also influence the thermal conductivity in experimental setups. The alignment of CNTs in the nanocomposites affects the overall conductivity. Composites with randomly aligned CNTs tend to have lower thermal conductivities. Thermal conductivities of the nanotube in the transverse directions can greatly influence the effective conductivity in a composite where CNTs are randomly dispersed. Dispersion of the CNTs in matrix material will influence the thermal conductivity in presence of interaction between the CNTs in the nanocomposite. Hence this study can extend on developing models which addresses random dispersions of the inclusions, effective thermal conductivities of non aligned inclusions and influence of thermal properties in transverse directions.

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BIOGRAPHICAL INFORMATION

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