MODELLING OF TENSILE MODULUS AND STRENGTH OF CARBON NANOTUBE REINFORCED POLYMER NANOCOMPOSITES

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It is hereby declared that the thesis titled **"Modeling of Tensile Modulus and Strength of Carbon Nanotube Reinforced Polymer Nanocomposites"** is authors's original work and has not been submitted for the award of any other degree or diploma.

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Md Saidul Islam

Author

DEDICATIONS

This work is dedicated to my beloved parents

Mrs Kazimon Begum

and

Alhaj Geda Mollah

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All praises to Almighty Allah, the most merciful, the most gracious and the most cordial, who bestowed upon the author the will, the ability, the vigor and the perseverance unless which it would have been impossible for the author to complete this research work.

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CONTENTS

ABSTRACT

Carbon nanotubes (CNTs) possessing extremely high stiffness, strength, and resilience would be the ultimate reinforcing materials for the development of polymer reinforced nanocomposites. CNTs are promising new materials for blending with polymers with potential to obtain low-weight nanocomposites of extraordinary mechanical, electrical, thermal and multifunctional properties. Unlike conventional fiber reinforced composites, there are wide variations in the diameter and length of the CNTs in the CNTs reinforced composites.

In this work a numerical model has been developed to calculate tensile modulus and tensile strength of randomly oriented short CNTs reinforced composites considering the statistical variation of diameter and length of the CNTs. According to this model, the whole composite is divided into several composite segments which contain CNTs of almost same diameter and same length. Tensile modulus and tensile strength of the composite is then calculated by weighted summation of the corresponding modulus and strength of each composite segment. Existing micromechanical approach for modeling of short fiber reinforced composites is modified to account for the structure of the CNTs to calculate the modulus and strength of each segmented CNTs reinforced composites. To consider the CNTs structure, multi-walled CNTs with and without intertube bridging have been considered. Statistical variations of the diameter and length of the CNTs are modeled by the normal distribution.

Effects of intertube bridging in multi-walled CNTs and variations of CNT diameter and length on the tensile modulus as well as tensile strength of the CNTs reinforced nanocomposites have been investigated using this developed model. Results obtained from this numerical model have also been compared with the available experimental results and the comparison concludes that the developed model can be used to predict tensile modulus and tensile strength of CNTs reinforced nanocomposites.

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CHAPTER 02

LITERATURE REVIEWS

2.1 INTRODUCTION

Carbon nanotubes (CNTs) have exceptional physical, mechanical, thermal and electrical properties [23-29]. However, the CNTs dimensions of the order of a few nanometer in diameter and few hundreds of micron length have put huge unsolved challenges before researchers. Perhaps, the most common challenging aspect is the CNTs dispersion into the polymer matrix since CNTs tend to agglomerate because of van der waals (vdW) forces. Most of the experimental investigations of CNTs reinforced polymer nanocomposites involve multi-wall carbon nanotubes (MWCNTs) instead of single-wall carbon nanotubes (SWCNTs) because of vdW interactions between tubes.

Composites materials of CNTs in polymeric matrices have potential as light weight and high strength fiber reinforced materials. For CNTs, to act as reinforcing fibers, significant load transfer must exist between the polymeric matrix and the CNTs. To date, both the mechanisms and magnitude of load transfer between polymeric matrices and CNTs remain unclear. Enhanced moduli in various polymer matrices indicate that CNTs may carry some of the load.

2.2 LITERATURE REVIEW

Future nano-structured reinforced polymer composite materials are expected to incorporate CNTs reinforcement either dispersed individually or as nano-filamentary reinforcement or ropes yielding unprecedented mechanical properties. Many believe that CNTs may provide the ultimate reinforcing materials for the development of a new class of nanocomposites [30]. The tensile properties and strength of CNTs reinforced nanocomposites have been demonstrated in several research works. Some of these investigations show that the load carrying capacity of CNTs in a matrix as well as the improvement of the tensile properties of the composites is significant and the CNTs reinforced composites have the potential to provide extremely strong and ultralight new materials.

Qian et al. [31] have reported that adding 1% of nanotubes to polystyrene matrix increases the overall tensile modulus (strength) by 42% (25%), indicating significant load transfer across the CNT-matrix interface. They have also observed via transmission-electron-microscope (TEM) graphs that the nanotubes were able to bridge the cracked surface of the composite once a crack was mitigated. The crack was nucleated at an area of low nanotube density and propagated towards a region with relatively low nanotube density. Pull-out of the nanotube was observed at a relatively large crack-opening displacement. Wagner et al. [32] have reported single nanotube fragmentation, under tensile stress, using nanotube-containing thin polymeric films. They have found that the interfacial shear strength (ISS) between the nanotubes and polymer could reach as high as MPa, which is at least one order of magnitude higher than that of conventional fiber-composites. Cooper et al. [33] have experimentally investigated the adhesion of to a polymer matrix. CNTs bridging across holes in an epoxy matrix were drawn using the tip of a scanning-probe microscope while recording the forces involved. Based on the experiment, an approximate calculation of the ISS of the CNT-polymer composite was performed. Their ISS values for MWCNTs very from 76-416 MPa for different interfacial area indicating that ISS of the CNT-polymer could be significantly higher than that of a conventional fiber-polymer interface. In another study, Barber et al. [34] have conducted a similar pull-out test of nano-tubes from a polymer and calculated the interface fracture energy from the measured pull-out force and embedded length. They have concluded that for smaller diameter nano-tubes there exists a strong interface. This strong interface with high ISS indicates that more loads will be transferred from the matrix to the nano-fiber through the interface and as a result reinforcement will be better.

Lourie et al. [35] have studies nanotube-polymer systems using TEM. Well-aligned bundles of SWNTs under tensile stress were observed to fracture in real time by TEM. The expansion of elliptical holes in the polymer matrix results in a tensile force in bridging nanotubes. The polymer matrix at both ends of the bundles deforms extensively under the tension force. The nanotubes fracture in tension within the polymer-hole region rather than in shear within the gripping region at the ends of the bundles. Direct observation of nanotube fracture in such a tensile test implies that stress is transferred from the surrounding matrix to the nanotubes through the nanotube-polymer interface, which is quite strong.

Mechanical, thermal and electrical properties of CNT-polymer nanocomposites have been studied by Haque et al. [36]. Nanocomposites of isotectactic polypropylene (iPP) and multi-walled carbon nanotube (MWCNTs) with different wt% of MWCNTs were prepared by multiple extrusions, followed by injection molding technique. Surface morphology of the composites was observed by a scanning electron microscope (SEM). Simultaneous wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) experiments were performed for structural analyses of the neat iPP and the nanocomposites. Mechanical properties such as tensile strength (*TS*), flextural strength (*FS*), percentage of elongation-at-break [*EB*(%)], flextural strain [*FS*(%)], Youngs's modulus (*Y*) and tangent modulus (*G*) were investigated by universal testing machine. SEM micrographs of the neat iPP and the nano-composites show that with the increasing MWCNTs content the surface become blackish appearance with good adhesion between iPP and MWCNTs. WAXS measurements reveal that an a- crystal is developed in the neat iPP along with lamellar structure having a long period of lamellar stakes of 150 A, which is observed by SAXS measurements. Inclusion of MWCNTs increases this long period and the intensity of SAXS patterns. Tensile strength, flexural strength, Youngs's modulus and tangent modulus are found to increase with increasing MWCNTs content. This increase can be attributed to the increased crystallinity of the nanocomposites. Also a decrease of *EB*(%) and *FS*(%) occurs with respect to the increase of MWCNTs content. Thermal analysis represents an increase of melting temperatures (T_m) and a decrease of degradation temperature (T_d) of the composites with increasing MWCNTs. AC electrical analyses shows a slight increase in both the dielectric constant and the conductivity of the sample with increasing MWCNTs content.

All of the above experimental observations indicate that the CNTs-polymer interfacial strength is high and significant load transfer occurs through the interface. However, some experimental observations indicate poor load transfer through a CNTs-polymer interface.

Schadler et al. [37] have studied MWNTs with epoxy polymer in both tension and compression. They observed a 6 cm^{-1} shift in compression and no shift in tension, implying that in tension load transfer to the MWNTs is negligible. This is attributed to two factors, the sliding of inner tubes within the outer tubes that prevent the load from being effectively transferred to all MWNTs layers and the extremely low interfacial shear stress between the tubes and the matrix arising from poor interfacial bonding. Barber et al. [38] have conducted MWNT pull-out from a polymer matrix using atomic force microscope. They have conducted several pull-out tests and calculated average ISS from the slop of the linear fit of the forces and corresponding interfacial areas data. They have found separation stress of 47 MPa indicating that CNTs do not significantly reinforce the polymer. Ajayan et al. [39] have also experimentally investigated the mechanical properties of CNTs reinforced polymer composites and they have reported that slipping of the tubes in the multi-wall nanotubes (MWNTs) limits load transfer from the polymer to the nanotubes.

The molecular dynamics (MD) approach has provided abundant simulation results for evaluating the mechanical properties of the CNT based polymer composites [40-42]. However, MD simulations are limited to very small length and time scales and cannot deal with the larger length scales in studying nanocomposites. Nanocomposites for engineering applications must expand from nano to micro, and eventually to macro length scales. Therefore, continuum mechanics models can be applied initially for simulating the mechanical responses of the CNTs in a matrix for studying the overall responses of CNT composites, before efficient large multiscale models are established.

The influence of chemical cross-links or intertube bridging between a SWNT fullerene nanotube and a polymer matrix on the matrix-nanotube shear strength has been studied using molecular dynamices simulations [40]. A (10,10) nanotube embedded in either a crystalline or amorphous polyethylene matrix is used as a model for a nonbonded interface (in the absence of intertube bridgigng). The simulations predict that shear strength and critical lengths required for load transfer can be enhanced and decreased, respectively, by over an order of magnitude with the formation of cross-links involving less than 1% of nanotube carbon atoms. At this level of chemical fictionalization, calculations also predict that there is a negligible change in tensile modulus for a (10,10) nanotube. Molecular mechanics simulations predict maximum frictional stresses from 18 to 135 MPa for sliding (10,10) nanotubes within single polymer chains.

Odegard et al. [43] used an equivalent continuum modeling method to model the local polymer near the nanotube and polymer/nanotube interaction. A suitable representative volume element (RVE) was chosen for the model. Molecular dynamics (MD) was used to simulate the interaction between the polymer (LaRC-SI) and (6,6) single-walled CNTs. In this work, the atomic lattice has been viewed as discrete masses assembled together with atomic forces that resemble elastic springs. The mechanical analogy of this model was a pin-jointed truss model in which each truss represents either a bonded or nonbonded atomic interaction. Next, the total strain energy of both truss model and the continuum model put equal under identical loading conditions. By applying proper loading conditions, it was possible to calculate all elastic constants (five sets of boundary conditions to determine five stiffness constants). Finally, traditional micromechanics models were utilized to determine the tensile modulus and strength of a polymer film reinforced by these fibers. Berhan et al. [44] presented a model to predict the upperbound moduli of ‘‘bucky paper’’ or nanotube sheet containing nanotube ropes with an emphasis on the effect of joint morphology. They obtained a sheet Young’s modulus ranging from 1% to 10% of the rope. Young’s modulus depending on the area fraction of the nanotube while their experimental results are fairly below these range (around 0.2% of the rope Young`s modulus).

Chen et al. [45] has proposed a 3-D continuum elasticity models for modeling the CNTs embedded in a matrix, in order to ensure the accuracy and compatibility between the models for the CNTs and matrix. There a method based on the elasticity theory for evaluating effective material properties of CNT-based composites using the RVE is established and cylindrical RVE are investigated. Formulas to extract the effective material properties from numerical solutions for the cylindrical RVEs under three loading cases are derived. Analytical results (extended rule of mixtures) based on the strength of materials theory to estimate the effective Young’s modulus in the axial direction, which can help validate the numerical solutions, are also derived for both long and short CNT cases in. Numerical results using the finite element method (FEM) for the cylindrical RVEs show significant increases of the stiffness in the CNT direction of the nanocomposites under various combinations of the CNT and matrix material properties. However, although cylindrical RVEs are easy to use, for which analytical solutions can be derived and efficient 2-D axisymmetric FEM models can be applied, they are the most primitive models and can lead to errors due to ignoring materials not covered by the cylindrical cells.

In the production processes, it is difficult to get isolated CNTs. CNTs have a propensity to aggregate to bundles or wrap together due to high surface energy. Moreover, it is also impossible to produce CNTs of a specific diameter and length. Usually in a sample of CNTs, there is a wide variation in CNTs diameter and length.

Ashrafi et al. [46] have investigated the elastic properties of twisted arrays of CNT based polymer composites using FEM. The tensile modulus and strength of the polymer composites reinforced by twisted CNTs array are also determined by using traditional micromechanics at low concentrations of CNTs, and the effects of different parameters such as the degree of the alignment, the twist angle and the volume fraction of the CNTs on the polymer composites are examined.

2.3 MOTIVATION OF THE PRESENT WORK

From the above literature review it is seen that there are some contradictory results regarding the reinforcement of the polymer matrix with the incorporation of CNTs. Moreover, in the literature on CNTs reinforced nanocomposites specially polymer nanocomposites, there is wide variation in the reported tensile modulus and tensile strength. Reported improvements in the tensile modulus and tensile strength are lower than the expected if the CNTs are assumed to act as reinforcing elements with tensile modulus and tensile strength of 1 TPa and 100 GPa respectively.

Discrepancies in the reported tensile modulus and tensile strength may be due to variation of CNTs diameter and length and the insufficient load transfer through the interface between CNTs and polymer matrix of the nanocomposites. The load transfer through the interface is affected by several factors. The vital factors are the morphology of the CNTs structure i.e. CNTs diameter, length and orientation. Therefore it is necessary to investigate their effects on the tensile modulus and tensile strength of CNTs reinforced polymer nanocomposites.

It is essential to investigate the effect of the morphology of the CNTs on the mechanical behavior of the CNTs reinforced polymer nanocomposites to fully realize the potentials of the CNTs-reinforced polymer nanocomposites in real engineering applications. Therefore, a numerical model to predict the tensile modulus and tensile strength of randomly oriented short CNTs reinforced polymer nanocomposites considering the variation of nanotube diameters and lengths simultaneously is necessary in designing actual CNTs reinforced polymer composites.

2.4 OBJECTIVES

The specific objectives of the present research work are as follows:

(a) To develop suitable analytical formula to determine the tensile modulus and density of equivalent solid fiber of realistic hollow CNTs.

(b) To develop a numerical model to calculate the tensile modulus and tensile strength of short, randomly oriented short CNTs reinforced polymer composites considering the variation of CNTs diameter and length.

(c) To investigate the effects of CNTs diameter and length on the tensile modulus and tensile strength of randomly oriented short CNTs reinforced polymer composites.

(d) To investigate the effects of interlayer cross-links or intertube bridging of CNTs on the tensile modulus and tensile strength of randomly oriented short CNTs reinforced polymer composites.

CHAPTER 03

MODELING OF NANOCOMPOSITE TENSILE MODULUS AND TENSILE STRENGTH

3.1 INTRODUCTION

Carbon nanofibers are molecular scale fiber of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibres known, with tensile modulus as high as 1 TPa and strength of up to 63 GPa. The nanofibres are relatively short, variable in diameter and length and imperfectly aligned. As discussed by Chou and Kelly [1,2], tensile modulus and strength of short, randomly oriented carbon nanofibre composites are complicated by the non-uniformity in fibre length, diameter and orientation. In this chapter, we will study modeling of the tensile modulus and strength of short, randomly oriented carbon nanofiber reinforced polymer composites. Also the fundamental equations and analytical formulas of the current research work has been derived.

3.2 CNTS STRUCTURE AND EQUIVALENT SOLID FIBER

It is important to consider the nanoscale structure of CNTs and how the nanotube interacts with the matrix to model the mechanical properties of the CNTs reinforced composite. CNTs can be pictured as being formed by rolling a graphite sheet into a cylinder. Various geometrical structures [47] can be formed depending on the orientation of the rolling axis. Two extreme orientations are called armchair and zigzag nanotubes. An armchair nanotube is formed when the sheet is rolled while keeping the rolling axis perpendicular to one of the hexagonal sides of the graphite lattice. In contrast, a zigzag nanotube is formed when the rolling axis is parallel to one hexagonal side. All other intermediate orientations will create another form of nanotube; being neither an armchair nor a zigzag nanotube. These nanotubes are called chiral nanotubes.

The ends of the nanotubes may be opened or closed, depending mainly on the production process by which the nanotube is produced. Usually, the ends of the nanotubes are closed off by half of a fullerene (i.e. a hemisphere). However, other sorts of cap structures such as a pencil cap, bowl cap, star cap etc. can also be produced at the nanotube ends. CNTs can also be classified as single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs), depending on the number of concentric walls. A SWNT consists of a single layer (or wall) of carbon atoms wrapped into a cylindrical shape. Typical diameters for SWNTs are on the order of 1 nm, while lengths are often on the order of micrometers. Both the diameter and the length of SWNTs are typically dependent on the particular technique used to produce them.

A MWNTs consists of several concentric layers of individual carbon nanotubes that are weakly coupled to each other through van der Waals forces. The spacing between the individual walls is on the order of 0.34 nm, slightly larger than the interlayer spacing in a graphite sheet. The diameter and number of walls comprising a MWNT are again dependent on the fabrication process. Their diameters are proportional to the number of concentric walls and the length, like that of SWNTs, can be of several micrometers.

3.2.1 Equivalent Solid Fiber for MWNTs without Intertube Bridging

To model the tensile modulus and tensile strength of CNTs reinforced composites, here we have considered MWNTs since these tubes with larger diameter are more stable compared to SWNTs. In case of MWNTs without intertube bridging, the outer layer of the tube will carry the entire applied load. Therefore, to determine elastic modulus and strength of the equivalent solid fiber, the load carrying capability of the outer layer of the nanotube must be applied to the entire solid cross-section of the equivalent solid fiber. An applied external force on the nanotube and the equivalent solid fiber (Fig. 3.1) will result in an iso-strain condition.

Therefore,

$$\varepsilon_{NT} = \varepsilon_{eqv} \quad (1)$$

Where ε is strain and subscripts NT and eqv refer to the nanotube and equivalent solid fiber, respectively.

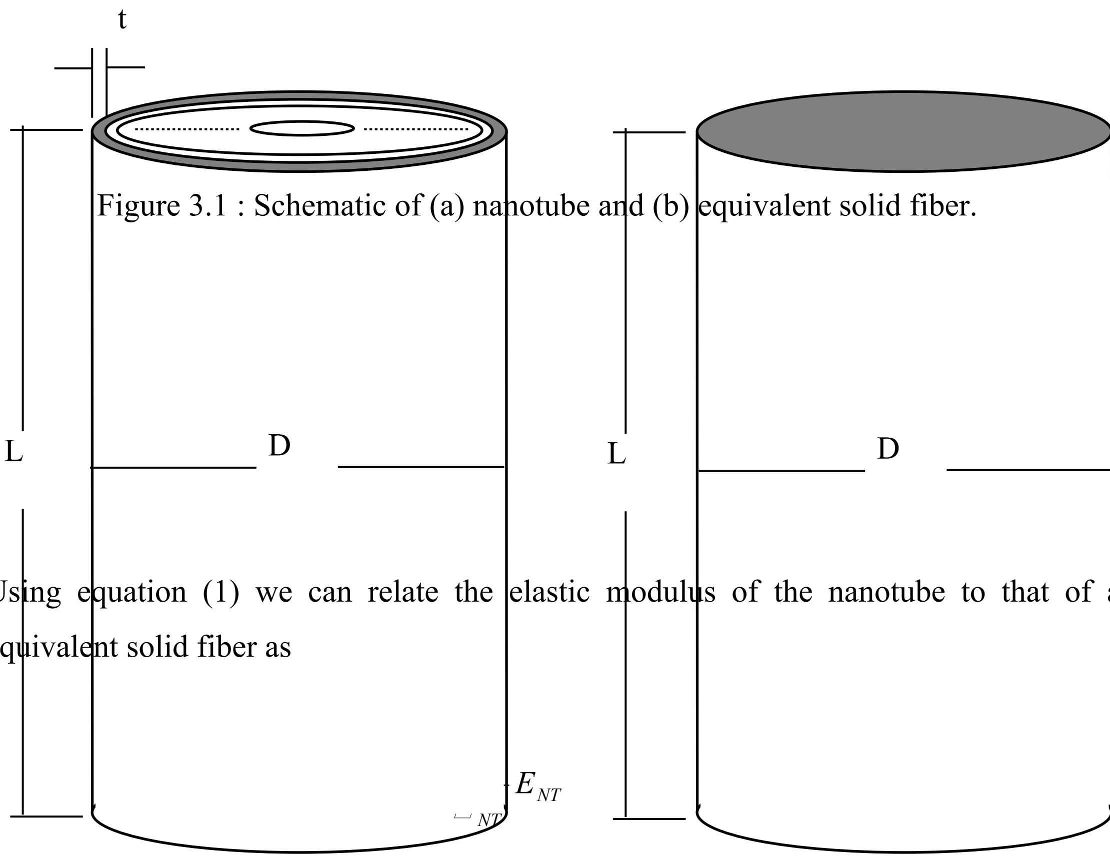


Figure 3.1 : Schematic of (a) nanotube and (b) equivalent solid fiber.

Using equation (1) we can relate the elastic modulus of the nanotube to that of an equivalent solid fiber as

$$E_{NT}$$

$$\sigma_{NT}$$

Where σ and E are stress and elastic modulus, respectively. Since the applied external force is the same, the modulus of the equivalent solid fiber can be expressed in terms of the ratio of their cross-sectional areas given as

$$E_{eqv} = \frac{A_{NT}}{A_{eqv}} E_{NT} \qquad (3)$$

Where, A is cross-sectional area. After substituting, the modulus of the equivalent solid fiber can be expressed in terms of elastic modulus of the nanotube, nanotube outer layer thickness (=0.34 nm) and nanotube outer diameter given as

$$E_{eqv} = \frac{4t}{D} E_{NT} \tag{4}$$

Where, t and D are nanotube outer layer thickness and outer diameter, respectively. Nanotube and its equivalent solid fiber will be able to carry the same ultimate load.

Therefore,

$$(F_{ult})_{NT} = (F_{ult})_{eqv} \tag{5}$$

Using equation (5) we can relate the strength of the nanotube to that of an equivalent solid fiber as

$$(\sigma_{ult})_{eqv} = \frac{A_{NT}}{A_{eqv}} (\sigma_{ult})_{NT} \tag{6}$$

After substituting, the strength of the equivalent solid fiber can be expressed in terms of that of nanotube, nanotube outer layer thickness and nanotube outer diameter given as

$$(\sigma_{ult})_{eqv} = \frac{4t}{D} (\sigma_{ult})_{NT} \tag{7}$$

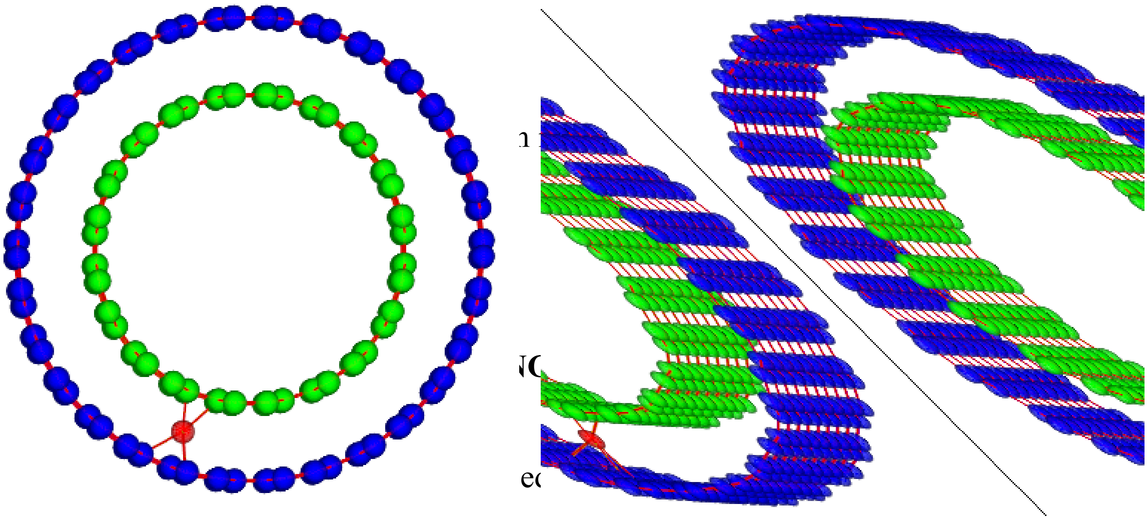
3.2.2 Equivalent Solid Fiber for MWNTs with Intertube Bridging

During the production and purification stages, some carbon atoms of MWNTs can be displaced from the hexagonal structure of the wall and be placed at the interstitial region of the CNTs creating intertube bridging as shown in Fig. 3.2 which is also called Frenkel pair defect [48]. Presence of intertube bridging tailors the mechanical properties of carbon nanostructures [49-51]. If there is perfect intertube bridging between adjacent layers of MWNTs so that relative sliding of the layers is restraint then the applied load will be shared by all layers of MWNTs. Tensile modulus and strength of the equivalent solid fiber of MWNTs with intertube bridging can be found from equations (8) and (9), respectively.

$$E_{eqv} = \frac{D^2 - D_i^2}{D^2} E_{NT} \tag{8}$$

$$(\sigma_{ult})_{eqv} = \frac{D^2 - D_i^2}{D^2} (\sigma_{ult})_{NT} \tag{9}$$

where D_i is the inner diameter of the nanotube.



(a) (b)

3.

A

completely perfect structure with specific diameter and length. Depending on the production process, CNTs are of different diameters and lengths with different imperfections (i.e., missing atoms in the wall of CNT, curved CNTs etc.). The distribution of nanotube diameter and length for a specific nanotube sample can be determined by measuring the outside diameter and length experimentally and the probability distribution of nanotubes for diameter and length $P(D,L)$ can be obtained.

With a view to model the composite mechanical properties, we study the volume fraction of carbon nanotubes within the composite. From the diameter and length distribution we can define the volume distribution of nanotubes $\square(D,L)$ as follows

$$\square(D,L) \square \frac{D^2 L P(D,L)}{\int_0^\infty \int_0^\infty D^2 L P(D,L)\, d(D)\, d(L)} \qquad (10)$$

Where, L is the length of CNTs.

The above volume distribution will need to be considered when calculating the overall nanocomposite properties.

3.4 DENSITY OF THE EQUIVALENT SOLID FIBER

For the conversion of weight fraction, measured when processing the nanocomposite, to volume fraction, needed for predicting the mechanical properties, we must know the density of the nanotubes and the matrix. For fibrous composites, the fiber volume fraction can be calculated based on the density of the constituents using following equation [11].

$$V_f = \frac{W_f}{W_f + (\rho_f / \rho_m) - (\rho_f / \rho_m) W_f} \qquad (11)$$

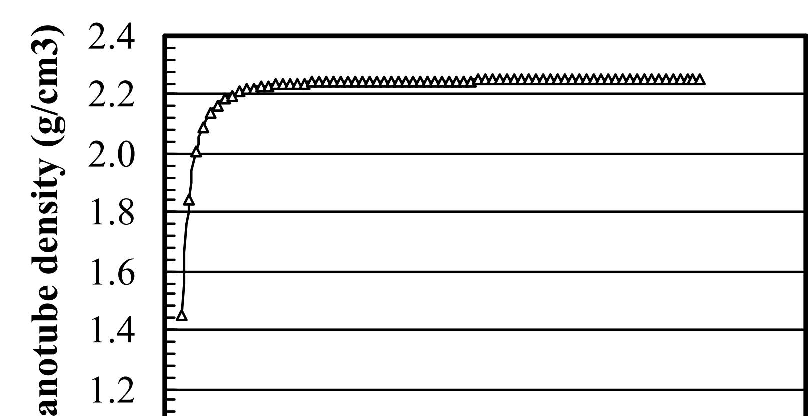
where, subscripts f, m and c refer to the fiber, matrix and composite, respectively.

From the measurements of nanotube outside and inside diameters, the density of the equivalent solid fiber can be calculated as

$$\rho_{eqv} = \rho_f = \frac{\rho_g (D^2 - D_i^2)}{D^2} \qquad (12)$$

Here, subscript g refers to fully dense graphite whose density is 2.25 g/cm^3.

Obviously, the density of the equivalent solid fiber will increase with the number of walls of the MWCNTs. The variation of density of equivalent solid nanotubes with outer diameters is shown in Fig. 3. 3.



the

$$\sigma_{eqv} = \sigma_f = \int_{D_L}^{D_U} \sigma_f(D)P(D) \qquad (13)$$

where, D_L and D_U are the lower and upper limit of the outer diameter of the nanotubes, $\sigma_f(D)$ is a function of nanotube outer diameter that can be obtained from the equation of the curve of Fig. 3.3, and $P(D)$ is the diameter distribution of the nanotubes.

3.5 CALCULATION OF NANOCOMPOSITE TENSILE MODULUS AND TENSILE STRENGTH

3.5.1 Tensile Modulus

A wide variety of models have been developed to predict the tensile modulus of fiber composites in terms of the properties of the constituent materials. Here we have used the most popular Halpin and Tsai [52] model according to which the tensile modulus of randomly oriented short fiber reinforced composites can be determined from the following equations

$$E = \left(\frac{3}{8}\right)E_{11} + \left(\frac{5}{8}\right)E_{22} \qquad (14)$$

Where,

$$E_{11} = E_m\left(\frac{1 + 2(L/D)\eta_L V_f}{1 - \eta_L V_f}\right) \qquad (15)$$

$$E_{22} = E_m \left(\frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right) \quad (16)$$

$$\eta_L = \frac{(E_f / E_m) - 1}{(E_f / E_m) + 2(L/D)} \quad (17)$$

$$\text{and, } \eta_T = \frac{(E_f / E_m) - 1}{(E_f / E_m) + 2} \quad (18)$$

By substituting equations (15) - (18) into (14) we can express the nanocomposite modulus in terms of the properties of the matrix and the nanotube reinforcement given as

$$E = \left(\frac{3}{8}\right) E_m \left[1 + 2(L/D) \left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2(L/D)} \right) V_f \right] \times \left[1 - \left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2(L/D)} \right) V_f \right]^{-1}$$
$$+ \left(\frac{5}{8}\right) E_m \left[1 + 2 \left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2} \right) V_f \right] \times \left[1 - \left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2} \right) V_f \right]^{-1}$$

(19)

Here, the value of $E_f (= E_{eqv})$ can be obtained from equation (4) and (8) for MWNTs without and with intertube bridging, respectively.

3.5.2 Tensile Strength

For a particular fiber strength as well as interfacial strength of the fiber-matrix interface, tensile strength of short fiber composites depends on length and diameter of the fiber. Tensile strength of randomly oriented short fiber composites can be obtained from the following equations [20]

$$(\sigma_{ult})_c = C_\theta (\sigma_{ult})_f \left(1 - \frac{L_c}{2L}\right) V_f + \sigma_m^{'} (1 - V_f), \text{ for } L \geq L_c \tag{20a}$$

$$(\sigma_{ult})_c = C_\theta \tau_i \frac{L}{D} V_f + (\sigma_{ult})_m (1 - V_f), \text{ for } L < L_c \tag{20b}$$

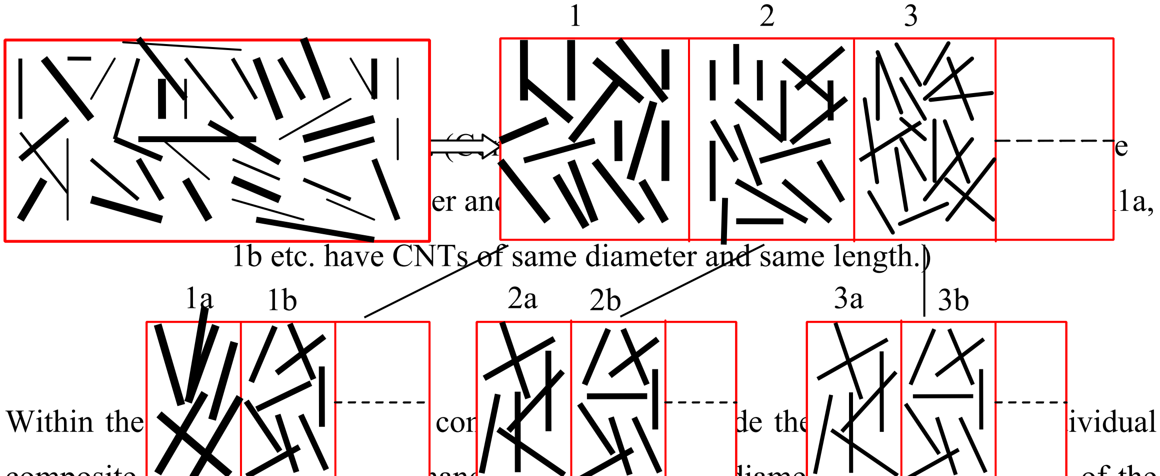
where L_c is the critical fiber length, C_θ is the fiber orientation factor, τ_i is the interfacial shear strength, $(\sigma_{ult})_c$ is the matrix ultimate strength, $(\sigma_{ult})_f$ is the fiber ultimate strength which is equal to $(\sigma_{ult})_{eqv}$ here and $\sigma_m^{'}$ is the matrix stress at the fiber failure strain. In case of CNTs reinforced polymer matrix composite, $\sigma_m^{'}$ will be equal to $(\sigma_{ult})_c$ if polymer experiences ultimate stress before CNTs and then polymer deforms plastically. Critical fiber length L_c can be obtained from the following equation [21]

$$L_c = \frac{(\sigma_{ult})_f}{2\tau_i} D \tag{21}$$

Equations (19) and (20) express the diameter and length dependence of the fiber (i.e., CNTs) reinforcement on the nanocomposite tensile modulus and tensile strength. It should be mentioned here that the strength of the CNTs can also be varied. Since we are concerned about the physical dimensions of the CNTs structure, strength of the CNTs is assumed constant in this study.

With distribution of nanotube diameter and length we can not use equations (19) and (20) directly to calculate the nanocomposite tensile modulus and tensile strength respectively. To accurately model modulus and strength of the composite, we must take into account the contribution to the overall tensile modulus and tensile strength for each nanotube diameter, length, and volume fraction that tubes of a specific diameter and length occupy within the composite. If nanotubes are uniformly dispersed and aligned throughout the matrix phase, the contribution of each diameter and length can be considered to act in parallel.

Therefore, the tensile modulus and tensile strength of the entire composite can be calculated as a summation of parallel composites over the range of nanotube diameter and length. The concept of parallel composites is illustrated in Figure 3.4.



… e … er an… 1a, 1b etc. have CNTs of same diameter and same length.)

Within the … cor… de the … ividual composite … Each of the N individual composite segments will have a specific tensile modulus and strength that depends on the local volume fraction of nanotubes at a given diameter and length. Tensile modulus and strengths of the whole composite can be expressed as a summation of the tensile modulus and strengths scaled by the partial volume of each nth composite segment given as

$$E_c = \sum_{n=1}^{N} v_n E_{c,n}(D_n, L_n) \tag{22}$$

$$(\sigma_{ult})_c = \sum_{n=1}^{N} v_n (\sigma_{ult})_{c,n}(D_n, L_n) \tag{23}$$

Where, $E_{c,n}(D_n, L_n)$ and $(\sigma_{ult})_{c,n}(D_n, L_n)$ are the tensile modulus and strength of the nth composite segment calculated using equations (19) and (20) respectively at the specific nanotube diameter and length and v_n is the partial volume of the nth composite segment given as

$$v_n = \frac{V_{c,n}}{V_c}, \tag{24}$$

where, V_c is the volume of the whole composite and $V_{c,n}$ is the volume of the segmented composite.

Here,

$$\sum_{n=1}^{\infty} v_n = 1 \tag{25}$$

To calculate the tensile modulus and strength at a given nanotube diameter and length using equation (19) and (20), the local fiber volume fraction at a given nanotube diameter and length can be calculated from the volume distribution of nanotubes (Eq. 10) given as

$$V_{NT}(D_n, L_n) = \frac{\int_{D_n}^{D_n+\Delta D_n} \int_{L_n}^{L_n+\Delta L_n} (V_{NT}\phi(D, L))d(D)d(L)}{v_n} \tag{26}$$

Graphical representation for the calculation of local CNTs volume fraction for an arbitrary distribution of CNTs diameter and length is shown in Fig. 3.5.

Figure 3.5 : Graphical representation for the calculation of local CNTs volume fraction.

CHAPTER 03

MODELING OF NANOCOMPOSITE TENSILE MODULUS AND TENSILE STRENGTH

3.1 INTRODUCTION

Carbon nanofibers are molecular scale fiber of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibers known, with tensile modulus as high as 1 TPa and strength of up to 63 GPa. The nanofibers are relatively short, variable in diameter and length and imperfectly aligned. As discussed by Chou and Kelly [1, 2], tensile modulus and strength of short, randomly oriented carbon nanofiber composites are complicated by the non-uniformity in fiber length, diameter and orientation. In this chapter, we will study modeling of the tensile modulus and strength of short, randomly oriented carbon nanofiber reinforced polymer composites. Also the fundamental equations and analytical formulas of the current research work has been derived.

3.2 CNTS STRUCTURE AND EQUIVALENT SOLID FIBER

It is important to consider the nanoscale structure of CNTs and how the nanotube interacts with the matrix to model the mechanical properties of the CNTs reinforced composite. CNTs can be pictured as being formed by rolling a graphite sheet into a cylinder. Various geometrical structures [47] can be formed depending on the orientation of the rolling axis. Two extreme orientations are called armchair and zigzag nanotubes. An armchair nanotube is formed when the sheet is rolled while keeping the rolling axis perpendicular to one of the hexagonal sides of the graphite lattice. In contrast, a zigzag nanotube is formed when the rolling axis is parallel to one hexagonal side. All other intermediate orientations will create another form of nanotube; being neither an armchair nor a zigzag nanotube. These nanotubes are called chiral nanotubes.

The ends of the nanotubes may be opened or closed, depending mainly on the production process by which the nanotube is produced. Usually, the ends of the nanotubes are closed off by half of a fullerene (i.e. a hemisphere). However, other sorts of cap structures such as a pencil cap, bowl cap, star cap etc. can also be produced at the nanotube ends. CNTs can also be classified as single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs), depending on the number of concentric walls. A SWNT consists of a single layer (or wall) of carbon atoms wrapped into a cylindrical shape. Typical diameters for SWNTs are on the order of 1 nm, while lengths are often on the order of micrometers. Both the diameter and the length of SWNTs are typically dependent on the particular technique used to produce them.

A MWNT consists of several concentric layers of individual carbon nanotubes that are weakly coupled to each other through van der Waals forces. The spacing between the individual walls is on the order of 0.34 nm, slightly larger than the interlayer spacing in a graphite sheet. The diameter and number of walls comprising a MWNT are again dependent on the fabrication process. Their diameters are proportional to the number of concentric walls and the length, like that of SWNTs, can be of several micrometers.

3.2.1 Equivalent Solid Fiber for MWNTs without Intertube Bridging

To model the tensile modulus and tensile strength of CNTs reinforced composites, here we have considered MWNTs since these tubes with larger diameter are more stable compared to SWNTs. In case of MWNTs without intertube bridging, the outer layer of the tube will carry the entire applied load. Therefore, to determine elastic modulus and strength of the equivalent solid fiber, the load carrying capability of the outer layer of the nanotube must be applied to the entire solid cross-section of the equivalent solid fiber. An applied external force on the nanotube and the equivalent solid fiber (Fig. 3.1) will result in an iso-strain condition.

Therefore,

$$\varepsilon_{NT} = \varepsilon_{eqv} \qquad (3.1)$$

Where ε is strain and subscripts NT and eqv refer to the nanotube and equivalent solid fiber, respectively.

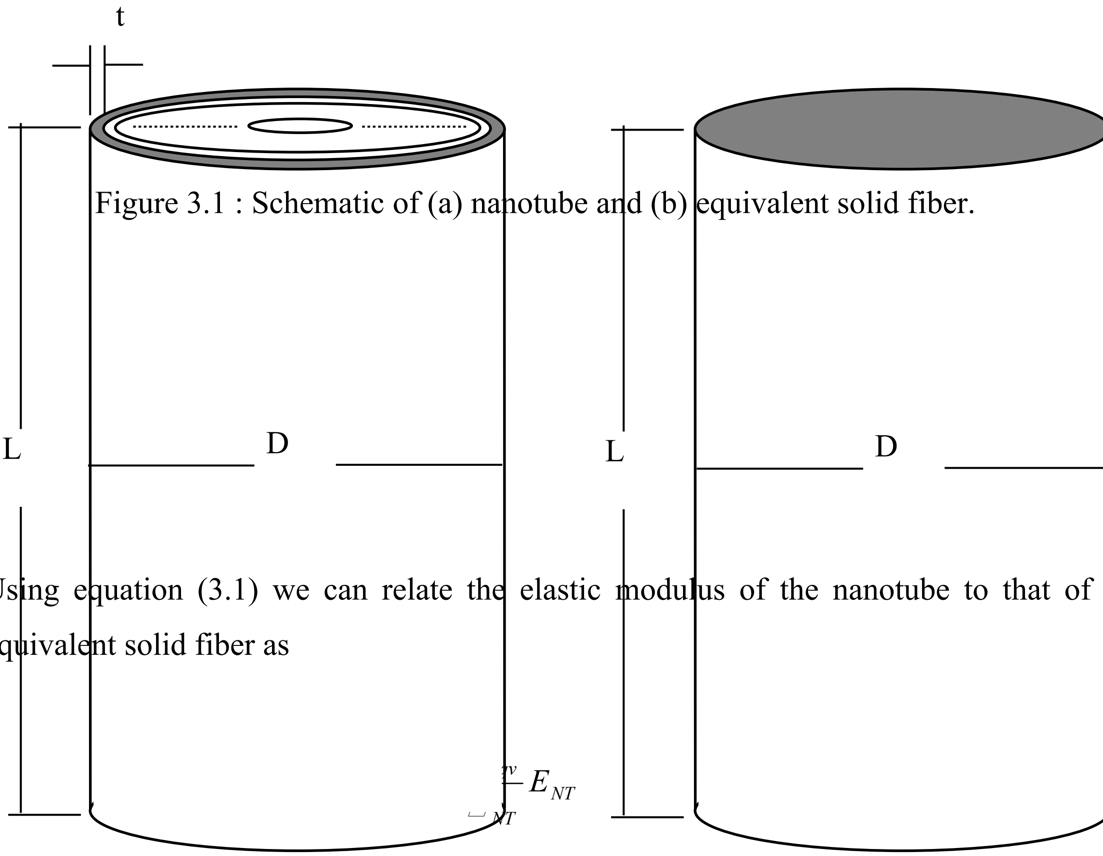


Figure 3.1 : Schematic of (a) nanotube and (b) equivalent solid fiber.

Using equation (3.1) we can relate the elastic modulus of the nanotube to that of an equivalent solid fiber as

$$E_{NT}$$

NT

Where σ and E are stress and elastic modulus, respectively. Since the applied external force is the same, the modulus of the equivalent solid fiber can be expressed in terms of the ratio of their cross-sectional areas given as

$$E_{eqv} = \frac{A_{NT}}{A_{eqv}} E_{NT} \qquad (3.3)$$

Where, A is cross-sectional area. After substituting, the modulus of the equivalent solid fiber can be expressed in terms of elastic modulus of the nanotube, nanotube outer layer thickness (=0.34 nm) and nanotube outer diameter given as

$$E_{eqv} = \frac{4t}{D} E_{NT} \tag{3.4}$$

Where, t and D are nanotube outer layer thickness and outer diameter, respectively. Nanotube and its equivalent solid fiber will be able to carry the same ultimate load.

Therefore,

$$(F_{ult})_{NT} = (F_{ult})_{eqv} \tag{3.5}$$

Using equation (3.5) we can relate the strength of the nanotube to that of an equivalent solid fiber as

$$(\sigma_{ult})_{eqv} = \frac{A_{NT}}{A_{eqv}} (\sigma_{ult})_{NT} \tag{3.6}$$

After substituting, the strength of the equivalent solid fiber can be expressed in terms of that of nanotube, nanotube outer layer thickness and nanotube outer diameter given as

$$(\sigma_{ult})_{eqv} = \frac{4t}{D} (\sigma_{ult})_{NT} \tag{3.7}$$

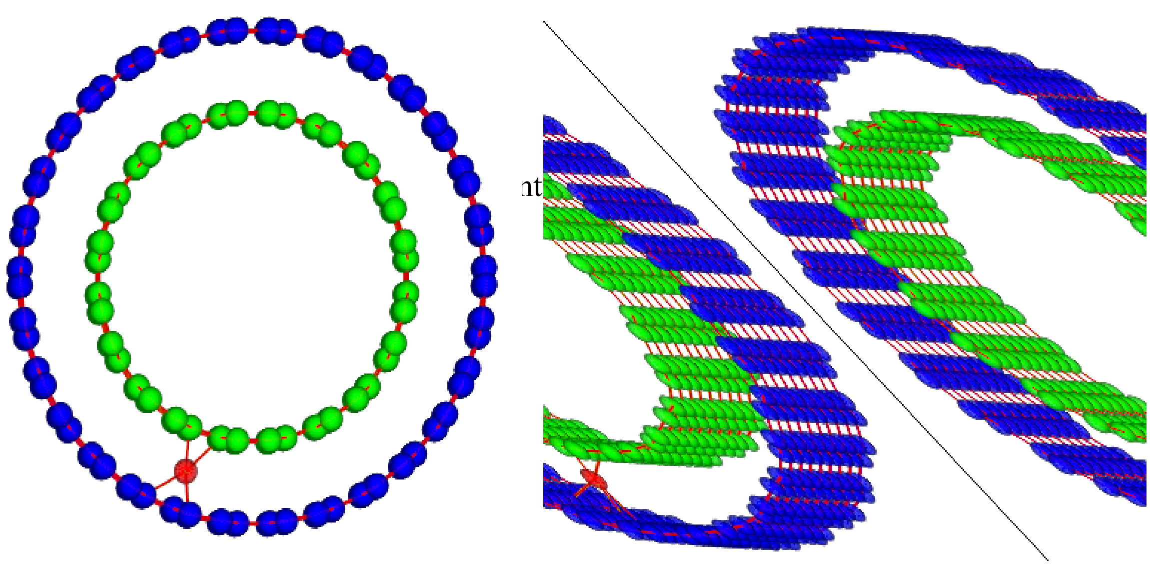
3.2.2 Equivalent Solid Fiber for MWNTs with Intertube Bridging

During the production and purification stages, some carbon atoms of MWNTs can be displaced from the hexagonal structure of the wall and be placed at the interstitial region of the CNTs creating intertube bridging as shown in Fig. 3.2 which is also called Freckle pair defect [48]. Presence of intertube bridging tailors the mechanical properties of carbon nanostructures [49-50]. If there is perfect intertube bridging between adjacent layers of MWNTs so that relative sliding of the layers is restraint then the applied load will be shared by all layers of MWNTs. Tensile modulus and strength of the equivalent solid fiber of MWNTs with intertube bridging can be found from equations (8) and (9), respectively.

$$E_{eqv} = \frac{D^2 - D_i^2}{D^2} E_{NT} \qquad (3.8)$$

$$(\sigma_{ult})_{eqv} = \frac{D^2 - D_i^2}{D^2} (\sigma_{ult})_{NT} \qquad (3.9)$$

where D_i is the inner diameter of the nanotube.



(a) (b)

3.3 NANOTUBE DIAMETER AND LENGTH DISTRIBUTION

Although CNTs can now be readily produced, it is quite difficult to produce CNTs with completely perfect structure with specific diameter and length. Depending on the production process, CNTs are of different diameters and lengths with different imperfections (i.e., missing atoms in the wall of CNT, curved CNTs etc.). The distribution of nanotube diameter and length for a specific nanotube sample can be determined by measuring the outside diameter and length experimentally and the probability distribution of nanotubes for diameter and length $P(D,L)$ can be obtained.

With a view to model the composite mechanical properties, we study the volume fraction of carbon nanotubes within the composite. From the diameter and length distribution we can define the volume distribution of nanotubes $\square(D,L)$ as follows

$$\square(D,L) \square \frac{D^2 LP(D,L)}{\int_0^\infty \int_0^\infty D^2 LP(D,L) d(D)\, d(L)} \qquad (3.10)$$

Where, L is the length of CNTs.

The above volume distribution will need to be considered when calculating the overall nanocomposite properties.

3.4 DENSITY OF THE EQUIVALENT SOLID FIBER

For the conversion of weight fraction, measured when processing the nanocomposite, to volume fraction, needed for predicting the mechanical properties, we must know the density of the nanotubes and the matrix. For fibrous composites, the fiber volume fraction can be calculated based on the density of the constituents using following equation [3.11].

$$V_f = \frac{W_f}{W_f + (\rho_f / \rho_m) - (\rho_f / \rho_m) W_f} \qquad (3.11)$$

where, subscripts f, m and c refer to the fiber, matrix and composite, respectively.

From the measurements of nanotube outside and inside diameters, the density of the equivalent solid fiber can be calculated as

$$\rho_{eqv} = \rho_f = \frac{\rho_g (D^2 - D_i^2)}{D^2} \qquad (3.12)$$

Here, subscript g refers to fully dense graphite whose density is 2.25 g/cm^3.

Obviously, the density of the equivalent solid fiber will increase with the number of walls of the MWCNTs. The variation of density of equivalent solid nanotubes with outer diameters is shown in Fig. 3. 3.

the

$$\sigma_{eqv} = \sigma_f = \int_{D_L}^{D_U} \sigma_f (D) P(D) \tag{3.13}$$

where, D_L and D_U are the lower and upper limit of the outer diameter of the nanotubes, $\sigma_f(D)$ is a function of nanotube outer diameter that can be obtained from the equation of the curve of Fig. 3.3, and $P(D)$ is the diameter distribution of the nanotubes.

3.5 CALCULATION OF NANOCOMPOSITE TENSILE MODULUS AND TENSILE STRENGTH

3.5.1 Tensile Modulus

A wide variety of models have been developed to predict the tensile modulus of fiber composites in terms of the properties of the constituent materials. Here we have used the most popular Halpin and Tsai [51] model according to which the tensile modulus of randomly oriented short fiber reinforced composites can be determined from the following equations

$$E = \left(\frac{3}{8}\right) E_{11} + \left(\frac{5}{8}\right) E_{22} \tag{3.14}$$

Where,

$$E_{11} = E_m \left(\frac{1 + 2(L/D)\eta_L V_f}{1 - \eta_L V_f} \right) \tag{3.15}$$

$$E_{22} = E_m \left(\frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right) \tag{3.16}$$

$$\eta_L = \frac{(E_f / E_m) - 1}{(E_f / E_m) + 2(L / D)} \qquad (3.17)$$

$$\text{and, } \eta_T = \frac{(E_f / E_m) - 1}{(E_f / E_m) + 2} \qquad (3.18)$$

By substituting equations (3.15) - (3.18) into (3.14) we can express the nanocomposite modulus in terms of the properties of the matrix and the nanotube reinforcement given as

$$E = \left(\frac{3}{8}\right) E_m \left[1 + 2(L/D)\left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2(L/D)}\right) V_f\right] \times \left[1 - \left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2(L/D)}\right) V_f\right]^{-1}$$
$$+ \left(\frac{5}{8}\right) E_m \left[1 + 2\left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2}\right) V_f\right] \times \left[1 - \left(\frac{(E_f / E_m) - 1}{(E_f / E_m) + 2}\right) V_f\right]^{-1} \qquad (3.19)$$

Here, the value of $E_f (= E_{eqv})$ can be obtained from equation (3.4) and (3.8) for MWNTs without and with intertube bridging, respectively.

3.5.2 Tensile Strength

For a particular fiber strength as well as interfacial strength of the fiber-matrix interface, tensile strength of short fiber composites depends on length and diameter of the fiber. Tensile strength of randomly oriented short fiber composites can be obtained from the following equations [3.20]

$$(\sigma_{ult})_c = C_{\theta}(\sigma_{ult})_f\left(1 - \frac{L_c}{2L}\right)V_f + \sigma'_m(1 - V_f), \text{ for } L \geq L_c \qquad (3.20a)$$

$$(\sigma_{ult})_c = C_{\theta}\tau_i \frac{L}{D} V_f + (\sigma_{ult})_m(1 - V_f), \text{ for } L < L_c \qquad (3.20b)$$

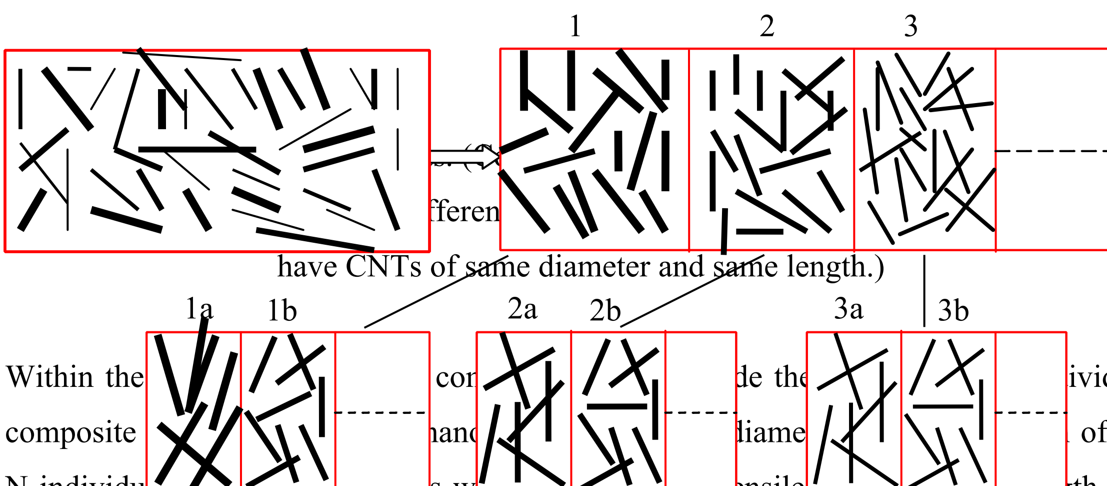
where L_c is the critical fiber length, C_{θ} is the fiber orientation factor, τ_i is the interfacial shear strength, $(\sigma_{ult})_c$ is the matrix ultimate strength, $(\sigma_{ult})_f$ is the fiber ultimate strength which is equal to $(\sigma_{ult})_{eqv}$ here and σ'_m is the matrix stress at the fiber failure strain. In case of CNTs reinforced polymer matrix composite, σ'_m will be equal to $(\sigma_{ult})_c$ if polymer experiences ultimate stress before CNTs and then polymer deforms plastically. Critical fiber length L_c can be obtained from the following equation [3.21]

$$L_c = \frac{(\sigma_{ult})_f}{2\tau_i} D \qquad (3.21)$$

Equations (3.19) and (3.20) express the diameter and length dependence of the fiber (i.e., CNTs) reinforcement on the nanocomposite tensile modulus and tensile strength. It should be mentioned here that the strength of the CNTs can also be varied. Since we are concerned about the physical dimensions of the CNTs structure, strength of the CNTs is assumed constant in this study.

With distribution of nanotube diameter and length we can not use equations (19) and (20) directly to calculate the nanocomposite tensile modulus and tensile strength respectively. To accurately model modulus and strength of the composite, we must take into account the contribution to the overall tensile modulus and tensile strength for each nanotube diameter, length, and volume fraction that tubes of a specific diameter and length occupy within the composite. If nanotubes are uniformly dispersed and aligned throughout the matrix phase, the contribution of each diameter and length can be considered to act in parallel.

Therefore, the tensile modulus and tensile strength of the entire composite can be calculated as a summation of parallel composites over the range of nanotube diameter and length. The concept of parallel composites is illustrated in Figure 3.4.



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have CNTs of same diameter and same length.)

Within the ... cor ... de the ... ividual composite ... nan ... diame ... of the N individu ... s w ... ensile ... th that depends on the local volume fraction of nanotubes at a given diameter and length. Tensile modulus and strengths of the whole composite can be expressed as a summation of the tensile modulus and strengths scaled by the partial volume of each nth composite segment given as

$$E_c = \sum_{n=1}^{N} v_n E_{c,n}(D_n, L_n) \tag{3.22}$$

$$(\sigma_{ult})_c = \sum_{n=1}^{N} v_n (\sigma_{ult})_{c,n}(D_n, L_n) \tag{3.23}$$

Where, $E_{c,n}(D_n, L_n)$ and $(\sigma_{ult})_{c,n}(D_n, L_n)$ are the tensile modulus and strength of the nth composite segment calculated using equations (3.19) and (3.20) respectively at the specific nanotube diameter and length and v_n is the partial volume of the nth composite segment given as

$$v_n = \frac{V_{c,n}}{V_c}, \tag{3.24}$$

where, V_c is the volume of the whole composite and $V_{c,n}$ is the volume of the segmented composite.

Here,

$$\sum_{n=1}^{\infty} v_n = 1 \tag{3.25}$$

To calculate the tensile modulus and strength at a given nanotube diameter and length using equation (3.19) and (3.20), the local fiber volume fraction at a given nanotube diameter and length can be calculated from the volume distribution of nanotubes (Eq. 3.10) given as

$$V_{NT}(D_n, L_n) = \frac{\int_{D_n}^{D_n+\Delta D_n} \int_{L_n}^{L_n+\Delta L_n} (V_{NT}\phi(D,L))d(D)d(L)}{v_n} \tag{3.26}$$

Graphical representation for the calculation of local CNTs volume fraction for an arbitrary distribution of CNTs diameter and length is shown in Fig. 3.5.

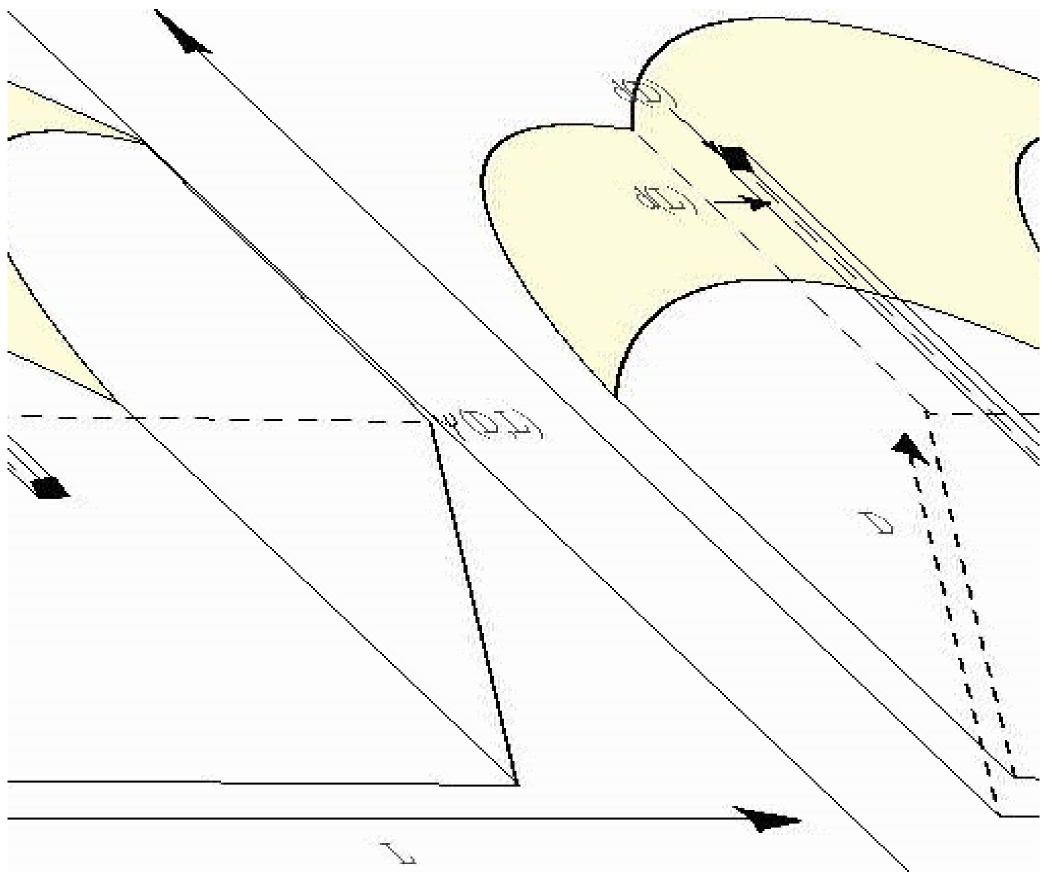

Figure 3.5 : Graphical representation for the calculation of local CNTs volume fraction.

CHAPTER 05

CONCLUSIONS AND RECOMMENDATIONS

5.1 INTRODUCTION

The use of CNTs in polymer materials is now being increasingly studied to produce advanced CNTs reinforced composites for aerospace, automotive, and military applications. However, super strong CNTs alone do not ensure super strong composites because the mechanical properties of CNTs reinforced composites are strongly influenced by the amount of load transfer from the matrix to the CNTs within the composites. Load transfer within the CNTs reinforced composites is influenced by the physical structure (i.e. diameter and length) of the CNTs and the interfacial conditions (i.e., with or without intertube bridging) between the CNTs and matrix.

In the literature on CNTs reinforced composites (specially polymer composites), there is wide variation in the reported tensile modulus and strength. Reported improvements in the tensile modulus and strength are lower than the expected if the CNTs are assumed to act as reinforcing elements with an tensile modulus of 1 TPa. Discrepancies in the reported tensile modulus and strength may be due to the insufficient load transfer through the interface between CNTs and polymer matrix of the composites. Load transfer through the interface is affected by several factors like CNTs diameter, CNTs length and interface condition. In this research investigation of their effects on the tensile modulus and tensile strength of CNTs reinforced polymer composites has been done. For that a numerical model has been developed to predict the tensile modulus and strengths of randomly oriented short CNTs reinforced composites considering the variation of CNTs diameters and lengths simultaneously which is necessary in designing real CNTs reinforced composites.

5.2 CONCLUTIONS

A numerical model has been developed for calculating the tensile modulus and tensile strength of short CNTs reinforced composites considering the variation of CNTs diameter and length. According to this model, the whole composite is divided into several composite segments which contain CNTs of almost same diameter and same length. Tensile modulus and tensile strength of the composite is then calculated by weighted summation of the corresponding tensile modulus and tensile strength of each composite segment. Existing micromechanical approach for modeling of short fiber composites is modified to account for the structure of the CNTs to calculate the tensile modulus and strengths of each segmented CNTs reinforced nanocomposites. For that purpose suitable analytical formula has been developed to calculate CNTs tensile modulus considering the CNTs variation of CNTs diameter and length. Statistical variations of the CNTs diameter and length are modeled by the normal distribution. The whole calculation is done by writing a FORTRAN program. Effects of intertube bridging in multi-walled CNTs and variations of CNTs diameter and lengths on the tensile modulus as well as tensile strength of the CNTs reinforced nanocomposite have been investigated using this developed model.

From the simulation results following conclusions have been drawn.

- Intertube bridging in the CNTs has significant effect on tensile modulus and tensile strength of the CNT reinforced composites. For particular CNTs diameter and length, composite having CNTs with intertube bridging has higher tensile modulus and tensile strength compared to the composite having CNTs without intertube bridging.

- With the increase of CNTs diameter tensile modulus and tensile strength of the composite reduce and this reduction is more significant for the CNTs with intertube bridging.

- With the increase of CNTs length tensile modulus and tensile strength of the composite increase and this increases is more significant for the CNTs with intertube bridging.

- Results obtained from this numerical model have been compared with the available experimental results and the comparison concludes that the developed model can be used to predict tensile modulus and tensile strength of CNTs reinforced composites provided physical dimensions of the CNTs, properties of the CNTs, matrix and CNT-matrix interface and information regarding the CNTs orientation are known.

5.3 RECOMMENDATIONS

The possible out come of this research work will give a vast knowledge about the effect of CNTs structural variations on the tensile modulus and tensile strength of CNTs reinforced composite. The developed model will be useful in designing randomly oriented short CNTs reinforced polymer composites and other CNTs based structural material. However, many research issues need to be addressed in the modeling of the tensile modulus and the tensile strength of CNTs reinforced polymer nanocomposites.

The developed model can be improved further including the following points in it.

- In CNTs reinforced polymer composites, it was assumed that the structure of CNTs is straight. However, in real case all CNTs in the CNTs reinforced composite are not straight. Some of the CNTs may be curved. This geometric imperfection can be included in the developed model.

- In this research, it was assumed that the strength of all CNTs is same. However, in real case the strength of individual CNT may vary. This strength variation can be included in this model.

Flow Chart (Algorithm)

(A) Flow Chart for calculation of CNTs Tensile Modulus:

Input: CNTs dia. distribution, CNTs length distribution, CNTs weight fraction, CNTs thickness, Graphite density, Matrix density, CNTs Modulus, Matrix Modulus.

↓

Calculate CNTs density using diameter distribution

↓

Calculate CNTs total volume fraction

↓

Calculate Equivalent solid fiber tensile modulus

↓

Calculate volume fraction of composite segments and CNTs local volume fraction.

↓

Determination of Tensile Modulus of Composite Segment

$$E = \left(\frac{3}{8}\right)E_m\left[1+2(L/D)\left(\frac{(E_f/E_m)-1}{(E_f/E_m)+2(L/D)}\right)V_f\right]\times\left[1-\left(\frac{(E_f/E_m)-1}{(E_f/E_m)+2(L/D)}\right)V_f\right]^{-1} + \left(\frac{5}{8}\right)E_m\left[1+2\left(\frac{(E_f/E_m)-1}{(E_f/E_m)+2}\right)V_f\right]\times\left[1-\left(\frac{(E_f/E_m)-1}{(E_f/E_m)+2}\right)V_f\right]^{-1}$$

↓

Determination of tensile modulus of whole composite:

$$E_C = \Sigma v_n E_{C,N}$$

↓

Output: CNTs weight fraction, composite tensile modulus (E_C)

(B) Flow Chart for calculation of CNTs Tensile Strength:

Input: CNTs diameter, CNTs length, CNTs Strength, Matrix Strength, Interfacial Shear Strength, Fiber Orientation Factor, CNTs Failure Strain, Matrix Failure Strain.

Calculate CNTs Density using CNTs diameter distribution

Total Volume Fraction of CNTs (Vcnt)

Calculate Equivalent Solid Fiber Strength

Calculate Critical Fiber Length, *(Lc)*

Calculate Volume Fraction of Composite Segment and CNTs Local Volume Fraction

Calculate Tensile Strength of Composite Segment

$$(\sigma_{ult})_c = C_0 (\sigma_{ult})_f \left(1 - \frac{L_c}{2L}\right) V_f + \sigma'_m (1 - V_f), \text{for } L \geq L_c$$

$$(\sigma_{ult})_c = C_0 \tau_i \frac{L}{D} V_f + (\sigma_{ult})_m (1 - V_f), \text{for } L < L_c$$

Calculate Tensile Strength of Whole Composite

$\sigma_C = \Sigma v_n (\sigma ult)_{C,N}$

Output: CNTs weight fraction, (Wcnt), Composite Tensile Strength, $(\sigma ult)_C$

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