B. TECH. PROJECT REPORT

On

Fabrication of Hybrid Epoxy Nanocomposite via an Innovative Dispersion Technique and Characterization of its Mechanical Properties

BY

Siddharth Jain (160003050)

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Fabrication of Hybrid Epoxy Nanocomposite via an Innovative Dispersion Technique and Characterization of its Mechanical Properties

A PROJECT REPORT

Submitted in partial fulfillment of the

Requirements for the award of the degree

Of

BACHELOR OF TECHNOLOGY

In

MECHANICAL ENGINEERING

Author:

Siddharth Jain

Supervisor:

Dr. Shailesh I. Kundalwal (Associate Professor)

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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CANDIDATE'S DECLARATION

I hereby declare that the project entitled **"Fabrication of Hybrid Epoxy Nanocomposite via an Innovative Dispersion Technique and Characterization of its Mechanical Properties"** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in Mechanical Engineering completed under the supervision of **Dr. Shailesh I. Kundalwal (Associate Professor, Mechanical Engineering)** IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

Signature and name of the student with date

CERTIFICATE by BTP Guide

It is certified that the above statement made by the student is correct to the best of my knowledge.

Signature of the BTP Guide with date and his designation

PREFACE

This report on “**Fabrication of Hybrid Epoxy Nanocomposite via an Innovative Dispersion Technique and Characterization of its Mechanical Properties** " is prepared under the guidance of Dr. Shailesh I. Kundalwal.

In this report, I have given an elaborate insight on the Finite Element (FE) methods for epoxy-carbon nanotube nanocomposites using simulation software and experimental methods for the homogeneous dispersion of carbon nanotubes in epoxy to enhance its mechanical properties. This nanocomposite can have important applications as an adhesive and as structural building blocks in aeronautics and aerospace industries.

I have tried my best to explain this content to the reader in a lucid and comprehensive manner. We have also added 3-D models and experimental results to make it more illustrative.

Siddharth Jain
B.Tech. IV Year
Discipline of Mechanical Engineering
IIT Indore

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I wish to thank **Dr. Shailesh I. Kundalwal** for his constant support and guidance in structuring this project and his valuable feedback throughout the course of this project. His overseeing the project meant there was a lot that I learnt while working on it. I thank them for their time and efforts.

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I would also like to acknowledge Mr. Anand Petare and his staff at **Central Workshop** of IIT Indore for providing their most sincere cooperation and guidance to our project. I would also extend my gratitude towards Mr. Deepak Rathore in the **Centre of Excellence in Gear Engineering (CEGE)** and Mr. Shubham Verma in the **Mechanics of Materials (MOM) Lab** for their assistance in the project.

I am really grateful to the Institute for the opportunity to be exposed to systemic research especially Dr. Shailesh Kundalwal's Lab for providing the necessary computing system and experimental apparatus to complete the project.

It is with their help and support that I was able to complete the experiments and technical report. Without their support, this report would not have been possible.

Siddharth Jain

B.Tech. IV Year

Discipline of Mechanical Engineering

IIT Indore

"Tired of lying in the sunshine staying home to watch the rain.
You are young and life is long and there is time to kill today.
And then one day you find ten years have got behind you.
No one told you when to run, you missed the starting gun."

~ Pink Floyd

ABSTRACT

The addition of carbon nanotubes (CNTs) in polymer matrix to produce multifunctional high strength polymer nanocomposites has been attracting great interest from research and industry communities due to their extraordinary properties. Experimental and numerical studies have demonstrated that the addition of a very small amount of CNTs into polymer matrix can significantly improve the mechanical properties of polymer nanocomposites. Understanding and prediction of the overall mechanical properties of the composites is essential for their engineering applications.

In this project, using finite element method, two-phase Representative Volume Element (RVE) was modelled with epoxy as matrix and CNT as fibre while three-phase RVE was modelled by incorporating ZrO_2 as interphase between the matrix and CNT. The effective elastic coefficients increase for both two phase and three phase nanocomposites with increase in the volume fraction of the CNT. Furthermore, the three-phase model shows better results for the effective elastic coefficients as compared to the two-phase model.

Further, cluster free homogeneous dispersion of multi-walled carbon nanotubes (MWCNTs) in the epoxy matrix was obtained by using Ultrasonication Dual Mixing (UDM) technique for 0%, 0.25%, 0.5% and 1% weight fractions of MWCNTs. A significant increase in the tensile strength and lap shear strength was observed as the weight fraction was increased from 0% to 0.5% followed by a decrease in the properties at 1%.

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To my family and friends for

all their love and support

Chapter 1

Introduction

1.1 Carbon Nanotubes (CNTs)

CNTs were discovered in 1991 by S. Iijima [1], and that started a revolution on the development of nanotechnology. Since then CNTs have been used in numerous fields such as sensors, nanometer sized semiconductor devices, probes and to fabricate conductive and high strength composites and also in biomedical application because of its extraordinary properties [2]. CNTs are sheets of graphitic carbon rolled to from tube like structures. CNTs have diameter in the range of a few nanometers. The chemical bonding of CNTs is composed entirely of sp^2 carbon– carbon bonds. This bonding structure – stronger than the sp^3 bonds found in diamond – provides CNTs with extremely high mechanical properties. They are one of the stiffest and strongest fibers and have remarkably unique characteristics. They display extraordinary properties with Young's modulus in the range of 1 TPa, tensile strength in the range of 200 GPa and strain 10-30% without breakage [3-4]. They are also thermally stable up to 2800 ºC in vacuum and 1000 times more electrically conductive than copper wires. CNTs have large aspect ratios, very low density, very high toughness and low chemical inertness.

Depending on the direction of the hexagons, CNTs can be classified into three types namely zigzag, armchair and chiral. 27 shows the different types of CNTs formed from a hexagonal graphene sheet. chiral CNT.

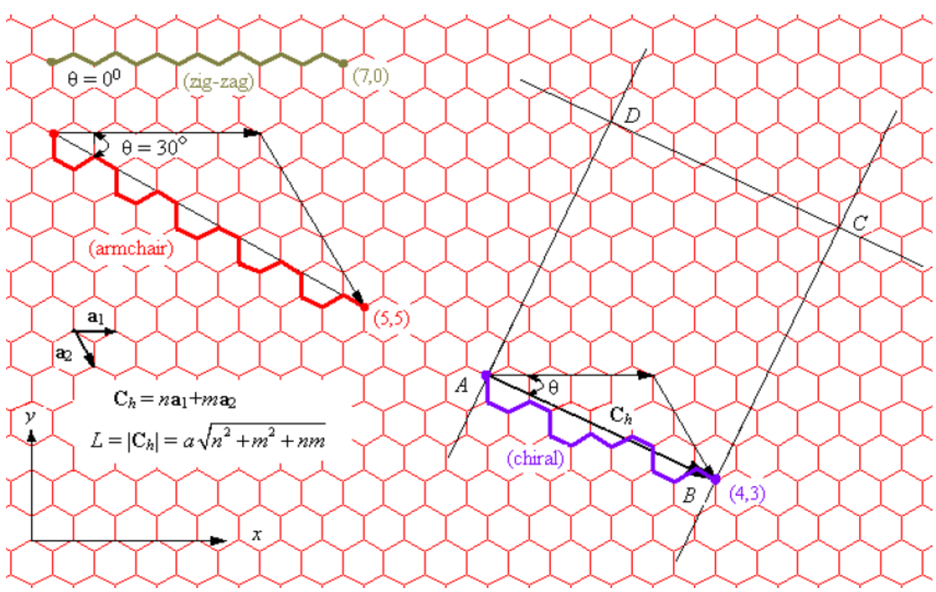

Figure 1 Formation of different types of CNTs [zigzag (7,0), armchair(5,5) and chiral (4,3) by rolling up a hexagonal graphene sheet.

CNTs can also be classified on the basis of number of CNT layer i.e. single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs). MWCNTs consist of nested layers of SWCNTs. The arrangement of graphitic sheets in SWCNT and MWCNT is shown in *Figure 2* and *Figure 3*.

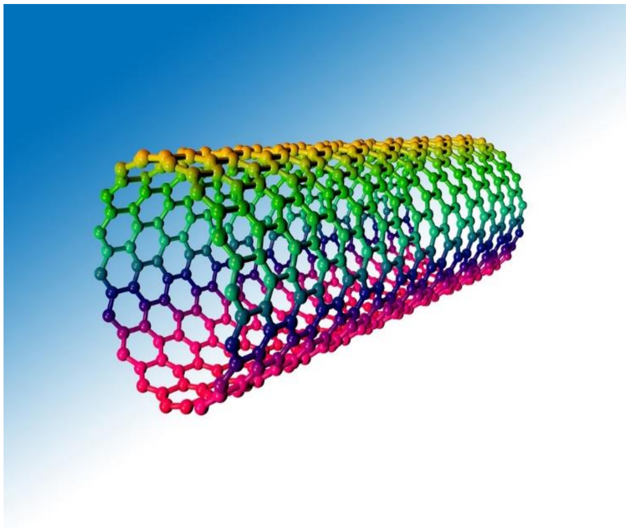

Figure 3 Single walled CNT (SWCNT)

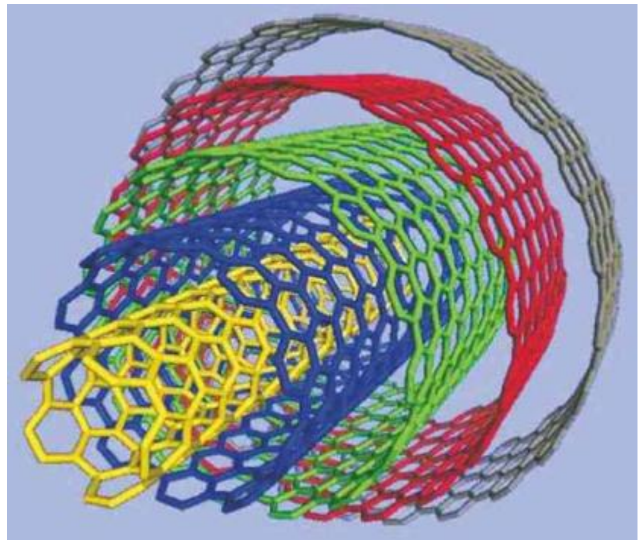

Figure 2 Multi-walled CNT (MWCNT)

CNTs can be used in various applications such as nanoelectronic devices, capacitors, sensors and actuators, fuel cells and solar cells, artificial muscles, multifunctional coating materials, electrodes or light emitting diodes (LEDs) and energy storage. Due to their extraordinary properties the most important application of CNTs is their use as reinforcements in structural composites leading to the development of CNT fiber reinforced composites.

1.2 Composites

A material that is being selected for application needs to fulfill a set of desired properties such as strength, stiffness, toughness, high corrosion and wear resistance, high chemical resistance, low weight and reduced cost. It is nearly impossible for a single material to fulfill all these desired properties. Composite materials can exhibit many of the above-mentioned properties. Composite materials are formed by combining two or more materials that have different properties. One of these materials acts as the matrix and the others act either as reinforcements or as interphase between the matrix and the reinforcement. These materials are bonded together to give a new multifunctional material having unique physical, mechanical, thermal and electrical properties.

The most important feature of composite materials is that their properties can be custom-made for their application. Thus, the use of composite materials can satisfy the need of application-based properties. By selecting a suitable combination of the matrix and the reinforcement material, a new material can be fabricated that precisely meets the demands of a particular application. Composites also provide the added advantage of being lightweight and strong. Composites also provide flexibility in design as they can be molded into complex shapes. The only disadvantage of using composite materials is that even though the resultant product is more efficient, the raw materials are costly. The low weight and high strength of composite materials increase their applications in automobile, aerospace and aircraft industries. Composites can be classified based on different forms of reinforcement as particle reinforced, flake reinforced or fiber reinforced. They can also be classified based on the type of matrix as metal matrix composites (MMCs), ceramic matrix composites (CMCs), carbon-carbon composites (CCCs) or polymer matrix composites (PMCs). The development of nanoparticle reinforced polymer composites is currently seen as one of the most promising approaches in the field of future engineering applications. In nanocomposites, at least one dimension of the reinforcement added is in the nanometer range.

1.3 CNT reinforced composites

CNT reinforced composites fall under the category of fiber reinforced composites. The matrix can be chosen to be any suitable metal, ceramic or polymer. There have been continuous efforts to improve the strengths of commonly used materials especially epoxy. CNTs give a solution to this problem because of their excellent chemical properties. CNT reinforced composites usually have high stiffness, high interfacial shear strength, high thermal and electrical conductivity, high thermal and chemical stability and high fracture toughness which makes them capable of being used in a wide variety of applications.

Studies show that the behavior of CNT reinforced nanocomposites depends on parameters like dispersion of the CNT particles in the polymer matrix, types of mixing methods and CNTs. One of the major challenges in the preparation of the CNT-epoxy nanocomposites is that the CNTs are difficult to disperse in a polymer matrix as they tend to agglomerate due to their high surface area, p-p interactions and high van der Waals forces of attraction. This leads to poor interfacial bonding between the matrix and the reinforcement. There are several mixing methods available for the dispersion of nanoparticles like the sol-gel method, extrusion, mechanical mixing and ultrasonication process. Among these techniques, the best results are obtained when ultrasonication mixing process is used for low weight fractions of CNTs added to the matrix [5-7]. The development of new manufacturing composites with high purity, geometrical identity, efficiency and low cost in making CNT reinforced composites more feasible.

1.4 Objectives

The current work is focused on fiber reinforced PMCs where carbon nanotubes are used as the reinforcing material and epoxy is used as the matrix. We choose epoxy resin as the polymer matrix because of its excellent properties such as chemical and corrosion resistance, high modulus and tensile strength, good dimensional stability, low shrinkage, absence of by products in curing, high adhesion, low cost and simplicity in processing. It has a wide range of potential application such as in electronics industry as an insulating coating for certain components, in aeronautics and astronautics industries as a key structural block and in the adhesives industry [8]. But the poor wear resistance, poor stiffness and poor fracture toughness of epoxy matrix limits its application where high strength and high fracture toughness are required. To overcome these difficulties, we add certain CNTs which leads to an increase in the overall mechanical properties of the epoxy matrix.

- The primary objective of this The primary objective of this study is to develop a multifunctional MWCNT-epoxy hybrid nanocomposite via a novel ultrasonication dual mixing technique(UDM). In UDM, the ultrasonicator is coupled with a magnetic stirrer with the aim of achieving homogeneous dispersion of the CNTs in the epoxy matrix.
- The mechanical properties of the prepare MWCNT-epoxy nanocomposite have been characterized using tensile test and lap shear test to verify the effect of UDM on the dispersion of CNTs.
- Finite element models have been developed for estimating the mechanical properties of the MWCNT-polymer nanocomposite.

Chapter 2

Literature Review

2.1 Numerical Analysis Literature

Since the discovery of carbon nanotubes (CNTs) (**Iijima, 1991**) [9], immense research work has been dedicated to find out their effective elastic properties. **Treacy *et al.* (1996)** [10] measured the amplitude of the intrinsic thermal vibrations of CNTs in a transmission electron microscope to estimate their Young's modulus. They reported the Young's modulus of CNTs to be of the order of terapascal (TPa). **Lu (1997)** [11] used an empirical force constant model to estimate the elastic properties of CNTs. He found that the elastic properties of single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) are not dependent on the radius, helicity and number of walls and the calculated values of the Young's modulus and shear modulus were close to that of diamond. **Popov *et al.* (2000)** [12] used analytical expressions to calculate Young's modulus, bulk modulus and Poisson's ratio of crystal lattices of single-walled CNTs. They reported some of these quantities to exhibit up to three different regimes of behavior which arise due to the Van der Waal's forces and the elastic forces in the tube. **Chang & Gao (2003**) [13] used an analytical molecular mechanics model with force equilibrium approach to study the variation of the elastic properties of SWCNTs with nanotube diameter. CNTs can be modelled as transversely isotropic materials **(Shen & Li, 2004)** [14]. Thus, the elastic properties of CNTs can be characterized by five independent elastic moduli. These five elastic moduli were first completely predicted by **Liu *et al.* (2005)** [15]. They implemented a hybrid atom-continuum model to investigate the bulk elastic properties of SWCNT bundles. They also found that the deformability of the tube cross sections play an important role in characterizing the tranverse moduli **Suzuki and Nomura (2007)** [16] employed molecular dynamics simulation using the well verified empirical potential for carbon and hydrocarbon molecules to obtain the elastic properties of SWCNTs under different strain regions**. Montazeri *et al.* (2010)** [17] computed the transverse-isotropic elastic properties of SWCNTs by combining molecular dynamics and continuum mechanics approach. These five independent elastic constants of a SWCNT in transverse directions are obtained by analyzing its deformations under four different loading conditions, namely, axial tension, torsion, uniform and non-uniform radial pressure.

With the aim of harnessing the excellent mechanical properties of CNTs, researchers have invested a lot of time in developing CNT reinforced polymer composites and estimating the effective elastic properties of the composites. For example, **Thostenson and Chou (2003)** [18] developed a micromechanical model of MWCNTs embedded in PMMA to understand the influence of size and structure of CNTs on the mechanical properties of the composite. They predicted the elastic modulus of the nanocomposite as a function of the constituent properties, reinforcement geometry and nanotube structure. **Odegard *et al.* (2003)** [19] used the equivalent-continuum modelling technique to study the effects of functionalization of CNTs on the elastic properties of CNT-polyethylene composites. The elastic properties of the composite system are predicted for various nanotube lengths, volume fractions, and orientations **Chen and Liu (2004)** [20] used a combination of continuum mechanics and finite element method to establish a square representative volume element (RVE) and calculated the elastic properties of CNT based composites. Formulas to extract the effective material constants from solutions for the square RVEs under two load cases are derived based on the elasticity theory. **Seidel and Lagoudas (2006)** [21] first obtained the in-plane elastic properties of graphene though a variety of micromechanics technique. They used these effective elastic properties to employ self-consistent and Mori-Tanaka methods to assess the effective elastic properties of aligned CNTs in composites. **Han and Elliott (2007)** [22] applied the molecular dynamics (MD) simulation and then used the constant-strain energy minimization method to evaluate the longitudinal and transverse elastic moduli of two different CNT reinforced polymer composites**.** classical molecular dynamics (MD) simulations of model polymer/CNT composites constructed by embedding a single wall (10, 10) CNT into two different amorphous polymer matrices: poly(methyl methacrylate) (PMMA) and poly{(m-phenylenevinylene)-co-[(2,5-dioctoxy-p-phenylene) vinylene]} (PmPV), respectively, with different volume fractions. **Tsai *et al.* (2010)** [23] implemented molecular dynamics (MD) simulation to develop the molecular structure of CNT-polyimide composite and then the elastic properties of the composite were evaluated using a three-phase micromechanical model. They suggested that the normalized non-bonded energy (non-bonded energy divided by surface area of the CNTs) is correlated with the extent of the interfacial interaction. **Pilli and Lu (2013)** [24] applied the Mori Tanaka (MT) method to develop equations for the elastic properties of epoxy matrix reinforced with cylindrical CNTs. **Wernik and Meguid (2014)** [25] studied both the linear and nonlinear properties of CNT reinforced structural adhesives by means of atomistic continuum modelling and nonlinear hybrid Monte Carlo finite element modelling methods. They observed considerable enhancement in the elastic properties of the composite for volume fractions ranging from 0.5% to 5%. **Alian *et al.* (2015)** [26] developed a multiscale modelling technique to determine the effective elastic moduli of CNT reinforced epoxy composites containing either well dispersed or agglomerated CNTs. They used MD simulations to determine atomic level elastic properties of a RVE. To study the effect of agglomeration, CNT bundles of different sizes were considered. Next, they implemented the Mori-Tanaka method to scale up the properties of the atomic structure to the microscale level, and used the outcome to investigate the effect of orientations and agglomeration of CNTs on the bulk elastic properties of the nanocomposite. **Arash *et al.* (2015)** [27] studied the variation of the Young's modulus of a CNT/PMMA composite with CNT volume fraction by developing a coarse-grained (CG) model of the composite. The simulation results revealed that the CG model is able to estimate the mechanical properties of the nanocomposites with high accuracy and low computational cost**. Gupta and Harsha (2016)** [28] created a square representative volume element (RVE) for a CNT polymer composite and used a multiscale finite element (FE) method to study the impact of vacancy defects on the elastic properties of the composite material. The three dimensional solid elements are used for matrix material. They studied the influence of the pinhole defects on the nanocomposite under axial load conditions. **Powar and Shirsat (2017**) [29] studied the influence of a broken CNT in the composite in the form of normal and shear stress redistribution surrounding the broken CNT. The small debonding between CNT and matrix near the broken CNT is treated as a crack. They used virtual crack closure technique (VCCT) to calculate the strain energy release rates. **Hassanzadeh-aghdam *et al.* (2018)** [30] employed a multiscale micromechanical modelling technique to analyze the elastic properties of randomly distributed polymer hybrid composites with CNT coated carbon fibers (CF) as reinforcement. They found that the contribution of CNTs to the elastic response of the hybrid composite in longitudinal direction can be neglected.

2.2 Experimental Methods Literature

A lot of experimental research has been conducted on CNT-epoxy composites by using various mixing techniques for a variety of weight fraction combination of CNT and epoxy. **Hsiao *et al.* (2003)** [31] dispersed different weight fractions of multi-walled carbon nanotubes in epoxy to produce toughened adhesives. The reinforced adhesives were used to bond the graphite fibre/epoxy composite adherents. Single lap joint samples were prepared and the average shear strengths were experimentally measured. **Song and Youn (2005)** [32] studied the effects of different dispersion states of carbon nanotubes (CNTs) on rheological, mechanical, electrical, and thermal properties of the epoxy nanocomposites. The dispersion states were altered depending upon whether a solvent was employed or not. **Zhou *et al.* (2007)** [33] infused MWCNTs in epoxy using a high intensity ultrasonic liquid processor and then cured the mixture using a high speed agitator. They characterized the mechanical and mechanical and thermal properties of the nanocomposite and found considerable enhancement in storage modulus and the glass transition temperature. **Halder *et al.* (2012)** [34] investigated the dispersion of nanoparticles and its influence on the mechanical properties by fabricating nanocomposites via mechanical mixing (MM) and ultrasonic dual mode mixing (UDMM). Mechanical mixing was employed by glass rod stirring and UDMM was employed by ultrasonic vibration along with magnetic stirrer. **Haldera *et al.* (2013)** [35] fabricated SiO_2-epoxy nanocomposite via MM and UDMM and investigated the dispersion of SiO_2 in epoxy and its effect on the tensile properties of the nanocomposite. **Ghosh *et al.* (2015)** [36] studied ultrasonic dual mixing involving ultrasonication with simultaneous stirring by axial flow impeller and ultrasonic waves were used to prepare well-dispersed graphene-PMMA composites and the mechanical properties were characterized. **Kumar *et al.* (2017)** [37] prepared a CNT-TiO_2 hybrid nanofiller to improve the interfacial bonding between epoxy and reinforcement. Hybrid nanofiller is introduced into epoxy and the mechanical and anti-corrosion properties of epoxy are studied. **Goyat *et al.* (2017)** [38] prepared high-performance epoxy-carbon nanotube (CNT) nanocomposites by simultaneous use of ultrasonication and mechanical stirring. The dynamic and static mechanical properties and wetting properties of the nanocomposites were investigated. A direct relation between the average roughness of the tensile fracture surfaces and the contact angle of the nanocomposites was identified with respect to the concentration of the CNTs. **Kumar *et al.* (2018)** [39] fabricated MWCNT-epoxy nanocomposite via MM and UDMM and investigated the dispersion of MWCNT in epoxy and its effect on the thermal and mechanical properties of the nanocomposite. **Kumar *et al.* (2018)** [40] obtained homogeneous and cluster free dispersion of MWCNTs in epoxy by using UDMM technique with axial flow impeller to develop toughened epoxy adhesives. The characteristics of the lap shear joint of MWCNT-epoxy adhesive on mild steel adherend are investigated.

Chapter 3

Methodology

3.1 Numerical Methodology

In this chapter, the elastic properties of CNT-epoxy composites have been calculated numerically by using square representative volume elements (RVEs) and finite element (FE) modelling technique. The effective elastic coefficients have been derived in two different scales namely meso and nano. In the meso scale, a two-phase RVE and a three-phase RVE have been defined and the effective elastic coefficients have been calculated for both the systems have been calculated. In the nano scale, the very small diameter of carbon nanotubes (~28 nm) has been taken into consideration and a two-phase dynamic explicit model has been defined to calculate the Young's modulus. The analysis was performed using hard boundary conditions.

3.1.1 Meso scale Square RVE and FE modelling

In the present work the RVE with a single CNT has been considered the effective elastic coefficients of CNT reinforced epoxy using the FE method. For the two-phase RVE, the CNT is placed at the center of the RVE and is surrounded by the matrix material. The RVE has been modelled for different volume fractions of the CNTs ranging form 0.1 to 0.5. The RVE was chosen to be of a unit dimension. For the three phase RVE, the CNT is placed at the center of the RVE and is surrounded by a layer of ZrO_2 which acts as an interphase material. The volume fraction of the CNT varied from 0.1 to and .5 and the volume fraction of the interphase layer was taken to be 0.5 times of the volume fraction of CNTs.

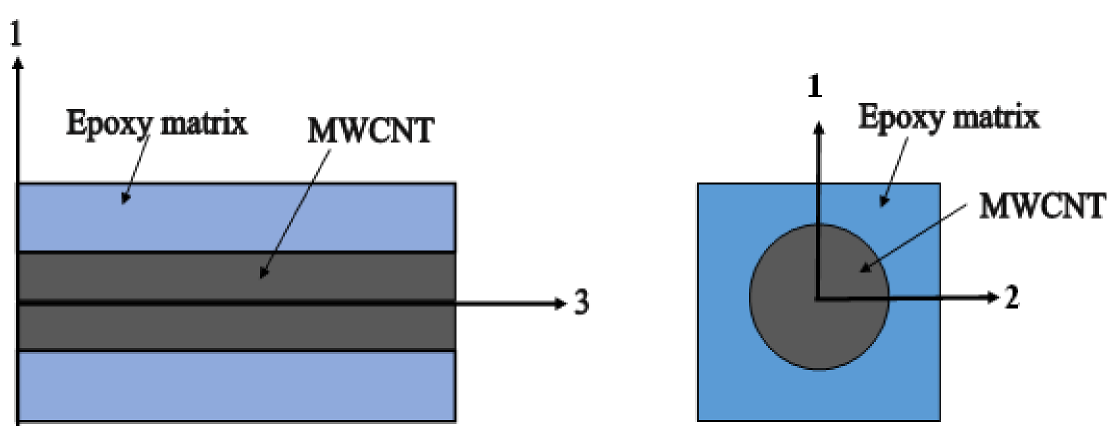

Figure 4 Side view and front view of a square RVE

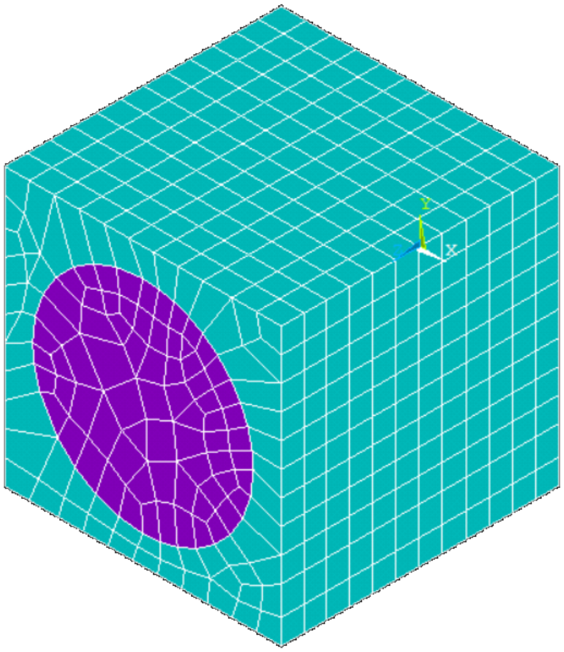

Figure 5 Isometric view of a two-phase RVE

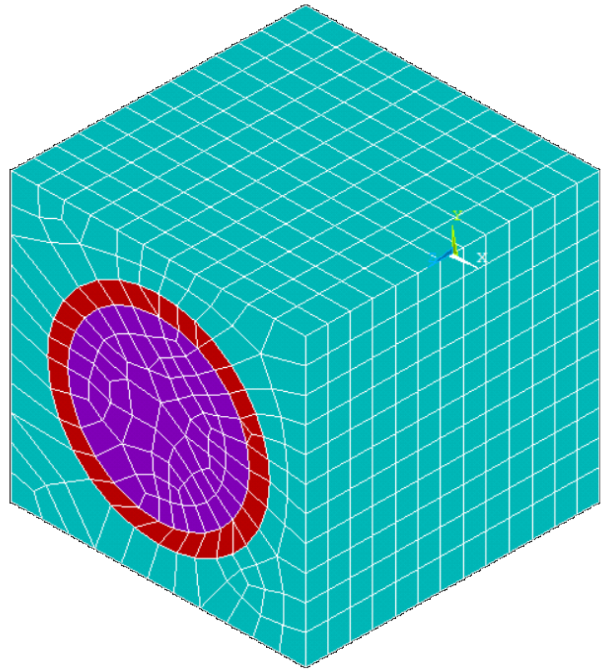

Figure 6 Isometric view of a three-phase RVE

Figure 7 and *Figure 8* and show the front view of the 3-D mesh of the two-phase and three-phase square RVE of CNT-epoxy composites. In the present study the *x-y* plane is taken as the transverse plane and the z-axis is taken as the axial direction. It has also been assumed that the CNT is aligned in the axial direction and that it is a MWCNT. Since the RVE is of unit dimension, the diameter of the CNTs depends on the volume fraction. In the case of the three phase RVE the volume fraction of the interphase of ZrO_2 is

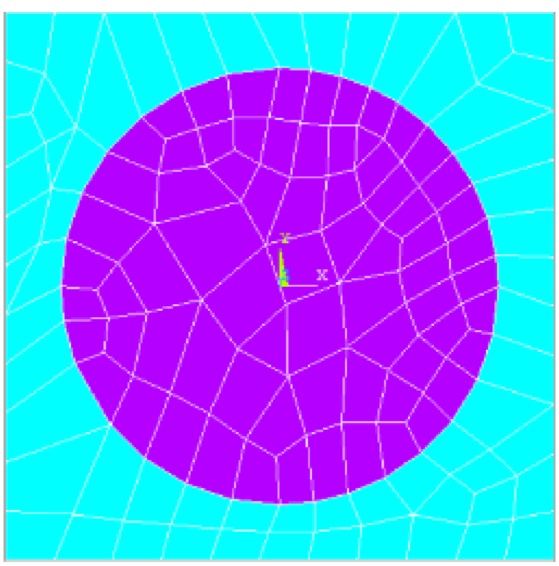

Figure 8 Front view of 3-D mesh of two-phase RVE

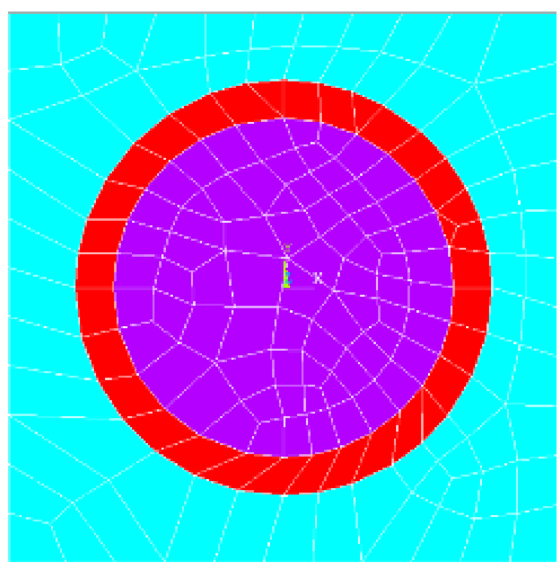

Figure 7 Front view of 3-D mesh of three-phase RVE

also dependent on the volume fraction of the CNTs. This numerical analysis was performed on ANSYS Mechanical APDL.

The meshing was done using the volume – smart size - sweep option for both two-phase and three-phase RVEs. For the two-phase RVE, SOLID186 element was used to define the behavior both the CNT and the epoxy matrix. For the three-phase material, SOLID186 element was used to define the behavior of CNT, epoxy matrix as well as the ZrO_2 interphase layer.

The material properties that were used are shown in *Table 1*.

Material	Young's modulus (GPa)	Poisson's Ratio
Epoxy	*3.5*	*0.33*
MWCNT	*1050*	*0.3125*
ZrO_2	*250*	*0.28*

Table 1 Material properties used in FE modelling

To calculate the effective elastic coefficients in the transverse and longitudinal direction, boundary conditions shown in were used.

S.No.	Elastic coefficient	Field displacement	Force field (N)	Displacement BCs
1	C_{33}	*Positive u_z / Face z^+*	-	*Zero normal displacements/ faces X+,X-,Y+,Y-,Z-*
2	C_{11}, C_{12}	*Positive u_x / Face x^+*	-	*Zero normal displacements/ faces X-,Y+,Y-,Z+,Z-*
3	C_{23}	*Positive u_y / Face y^+*	-	*Zero normal displacements/ faces X+,X-,Y-,Z+,Z-*

Table 2 Boundary conditions for two-phase and three-phase FE models

3.1.2 Nano scale RVE and FE modelling

The above-mentioned method was based on static solutions of the FE model and did not account either for the size of the CNTs or the non-linearity of the epoxy matrix. To account for the non-linearity of epoxy and calculate the Young's modulus of the CNT-epoxy composite, another FE model was created based on the dynamic explicit solver. In the dynamic explicit solver the load is applied as a function of time.

This nanoscale model and also took in consideration the very small diameter of CNTs which was taken as 28 nm. The CNT was placed at the center of the RVE and was assumed to be aligned in the axial direction. The two phase RVE was modelled for 0.1 weight percent of CNT and the side of the square was taken as 815 nm. The interaction between the CNT and epoxy was assumed to be cohesive but this behavior could not be directly applied due to limitations in the simulation software while using the dynamic explicit solver.

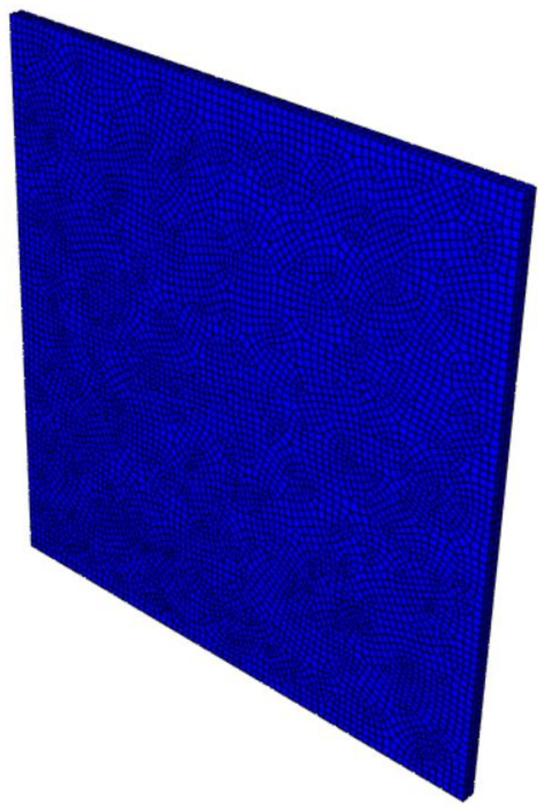

Figure 9 Nanosclae RVE with diameter of CNT as 28 nm

To overcome this challenge a thin layer of cohesive elements was inserted between the matrix and the epoxy. *Figure 9* shows the isometric view of the square RVE.

To account for the non-linearity of the epoxy matrix the elastic properties epoxy were defined by using the Drucker-Prager (DP) hardening method. The DP hardening is a simple modification of the Von Mises criteria. It is effective because it considers the influence of hydrostatic stress on a system. It is represented by the equations

$$F=t-p\tan\beta-d=0 \quad (1)$$

$$t= 12\ q\ 1+1K-1-\ 1Krq3 \quad \text{, where} \quad (2)$$

- β is the slope of the linear yield surface in P-t stress plane
- d is the cohesion yield stress

- K = ratio of the yield stress in triaxial tension to that in triaxial compression
- r = third stress invariant of deviatoric stress
- q = Von-Mises stress
- p = hydrostatic stress

The analysis was performed on ABAQUS simulation software and the input parameters to model the DP hardening were β and K. The meshing shown in *Figure 9* was done using hex elements, swept across the volume of the RVE. The element type used for the CNT and epoxy was C3D8R and number of elements used was 16526.

3.2 Experimental Methodology

The epoxy used was epoxy resin Epofine 1564 along with the hardener epoxy hardener Finehard 3486 and they were obtained from Fine Finish Organics Pvt. Ltd. Acetone was procured from Finar Chemicals. Liquid Silicone Rubber LSR-2 Part A and Part B were obtained through online retailers. Mild stainless steel sheet to form the patterns for fabricating the moulds and aluminium sheet for lap shear test specimen were obtained from the local markets.

Mild steel sheet was used to create the patterns in the shape of tensile specimen, three-point bend specimen and DMA specimen based on ASTM standards. The specimen were cut by using Wire Electrical Discharge Machining (W-EDM) to achieve high precision in creating the patterns. Silicone Rubber moulds were fabricated using these patterns. Epoxy is a very strong adhesive and sticks to metallic surfaces, so the usage of metallic moulds was no possible in creating the specimen. To fabricate the moulds the patterns were placed in a container of appropriate and silicon oil was applied on the patterns as well as the base and walls of the container for easy removal of the mould from the container and to separate the patterns from the moulds. Liquid silicone rubber LSR-2 part A was mixed with was mixed with 3% LSR-2 part B and quickly poured into the container. This was then left to cure in a hot air oven at 40 ºC overnight. *Figure 10* shows the silicone rubber moulds that were prepared.

Figure 10 Silicone rubber molds for tensile, DMA and three point bend specimen

After the preparation of the mould, the MWCNT/epoxy mixture was prepared. MWCNTs were added in epoxy in the desired weight fraction with 10% acetone and then mixed initially by stirring with a glass rod for 2-3 minutes. Epoxy is a very viscous liquid, which makes the mixing of MWCNTs in epoxy difficult. The viscosity of epoxy along with the strong Van der Waal’s forces of attraction in the CNTs assists in the agglomeration of CNTs, which is undesirable. To ease the mixing process, acetone is added to the mixture. Then ultrasonic waves generated from 19 mm diameter titanium alloy (Ti- 6Al-4V) tip of ultrasonic processor of maximum output power of 750 W with a constant frequency of 20 kHz and magnetic stirring is applied on 50 ml volume of MWCNT-epoxy resin mixture and this process is called ultrasonic dual mode mixing (UDMM) process. In this process, 60 % amplitude of power system with pulse (5 sec on and 5 sec off) is used for 1 hour. To control the temperature at 50 °C during processing, the beaker is kept in an ice bath. After the process the mixture is placed in a hot air oven at 80 °C for 24 hours to remove the acetone. After the process, the required amount of hardener (30 wt.%) is homogeneously mixed in MWCNT-epoxy mixture followed by vacuum degassing to remove the air entrapped during mixing. Specimen for tensile are prepared by pouring the resulting nanocomposite slurry into the silicon rubber moulds that were fabricated and placed in hot air oven for 12 hours at 50°C to complete the curing. After the curing, the specimen obtained were used to characterize the mechanical properties of the MWCNT-epoxy nanocomposite by performing tensile and lap shear strength tests. The parameters implemented in the UDMM technique were as shown in *Table 3* and *Table 4*. *Figure 11* shows the step by step flow of the experimental process.

Table 3 Parameters for ultrasonicator in UDMM

Parameters	**Value**
Amplitude	60% of total power output (750 W) of the ultrasonicator
Pulse	5 seconds ON and 5 seconds OFF
Maximum Probe Temperature	50 ºC
Frequency	20 KHz
Total Duration	1 Hour

Table 4 Parameters for magnetic stirrer in UDMM

Parameters	**Value**
RPM	300
Heating	OFF

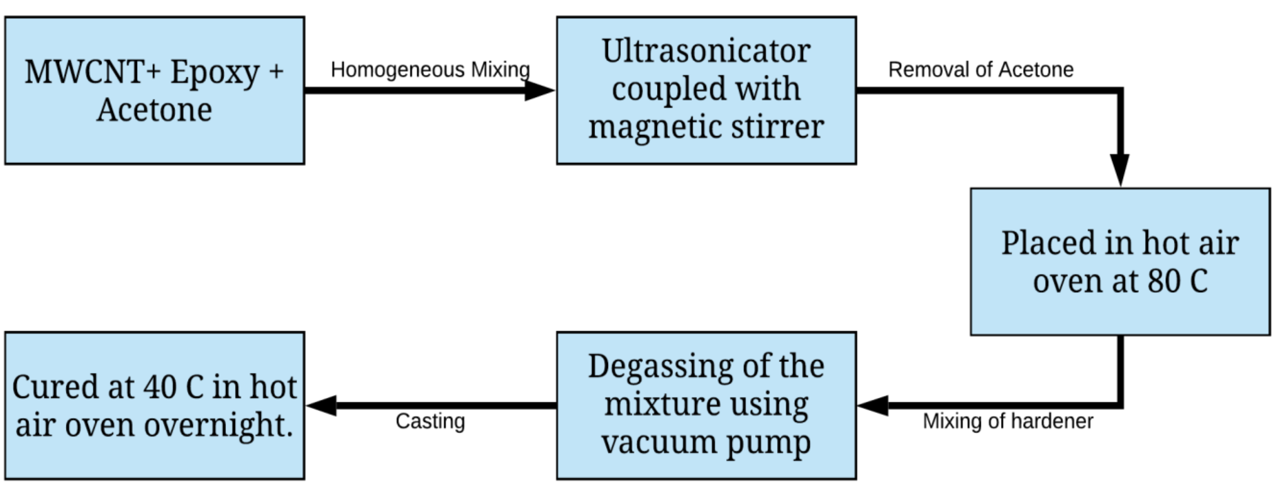

Figure 11 Steps involved in fabricating MWCNT-epoxy nanocomposites

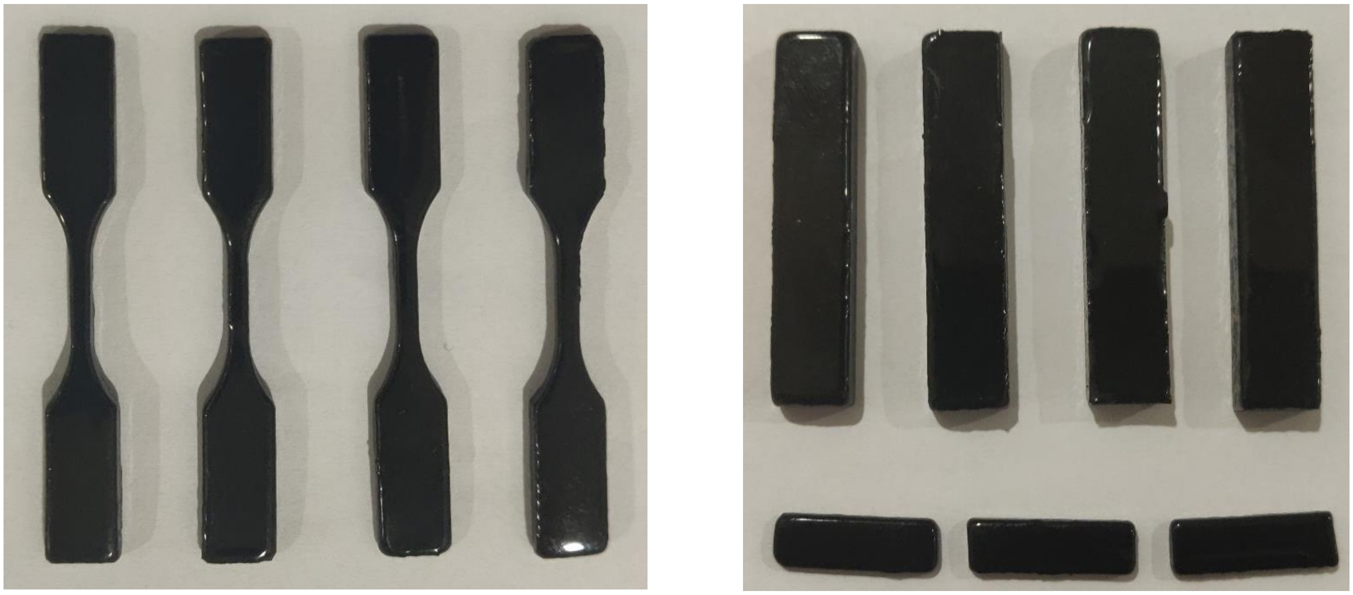

Figure 12 Tensile, DMA and three-point bend specimen for 0.5 wt. % MWCNT

Figure 13 Tensile, DMA and three-point bend specimen for pure epoxy

The mechanical properties of the nanocomposites that were prepared were characterized by performing the following tests on the prepared specimen.

3.2.1 Tensile Test (ASTM D-638)

Tensile testing of the neat epoxy and its nanocomposite specimen is carried out by following the ASTM D-638(V) standard. The dumbbell-shaped tensile specimen are tested by a Universal Testing Machine (UTM), at a crosshead speed of 1 mm/min at ambient conditions. The stress-strain curves of tensile test specimens are used for determination of tensile strength, elastic modulus, strain-to-break % and area under the stress-strain curve (or toughness). The toughness is obtained from the area under the stress-strain curve and the elastic modulus is estimated from linear fitting of initial portion of the stress-strain curve until strain of 0.3%. At least three replicate specimens are tested and their mean values used to plot the results.

3.2.2 Lap Shear Strength Test (ASTM D-1002)

The mechanical performance of the adhesive joints is studied by single lap shear testing. During the test, the cross-head speed of the UTM machine is 1 mm/min and specimen are gripped on an alignment tab. The lap shear strength (=σ_s) of joints with various adhesives is determined according to the expression σ_s = (N/X)* Y, where N stands for the failure load (Newton), X stands for the width of the adhesive joint (mm), and Y stands for the length of adhesive joint (mm). The results reported are the average of at least four measurements and the stress–strain plot is recorded up to fracture of the adhesive joint.

Chapter 4

Results and Discussions

4.1 Numerical Analysis Results

The numerical analysis of both the meso scale RVE and the nano scale RVE yielded valuable information on the behavior of epoxy on addition of CNTs. The results for both the models have been discussed in the following subsections.

4.1.1 Meso scale RVE

Both two-phase and three-phase composites were modelled at the meso scale and their effective elastic properties were determined. Both the models showed considerable increase in the elastic properties of epoxy with increasing weight percentage of CNTs. Further, the obtained values for the two-phase and three-phase composites were compared. The results have been plotted as shown in the following graphs.

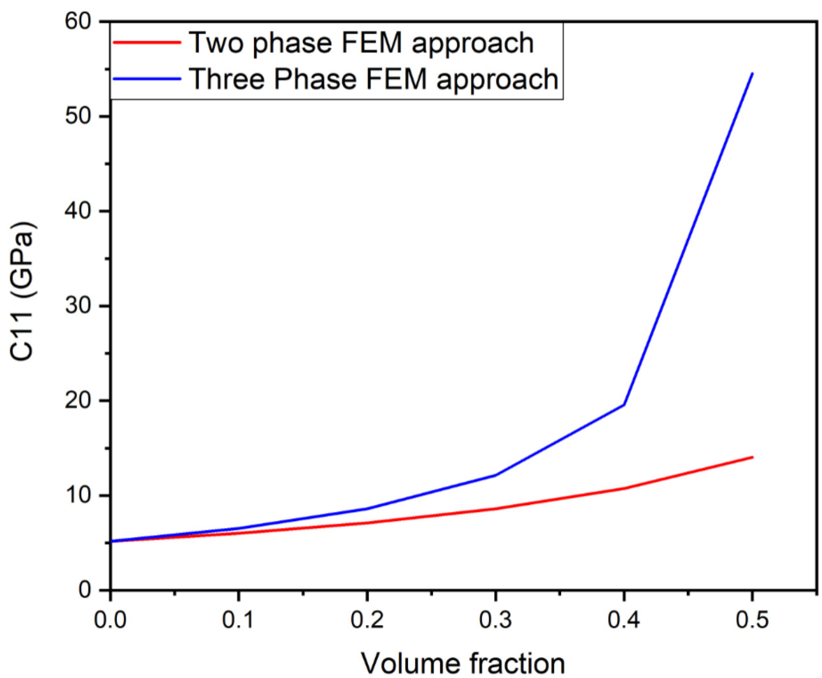

Figure 14 Variation of the effective elastic coefficient C11 of composites against MWCNTs volume fraction.

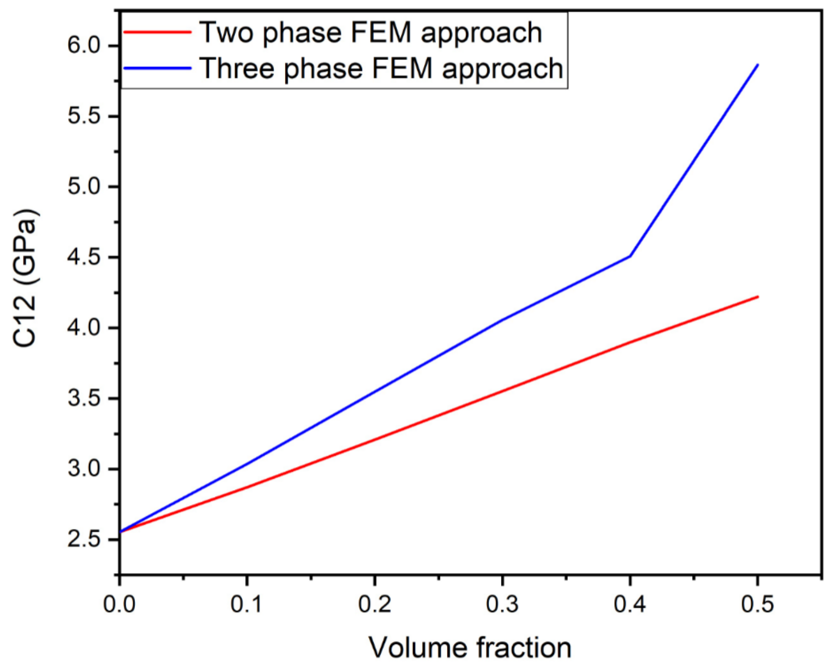

Figure 15 Variation of the effective elastic coefficient C12 of composites against MWCNTs volume fraction.

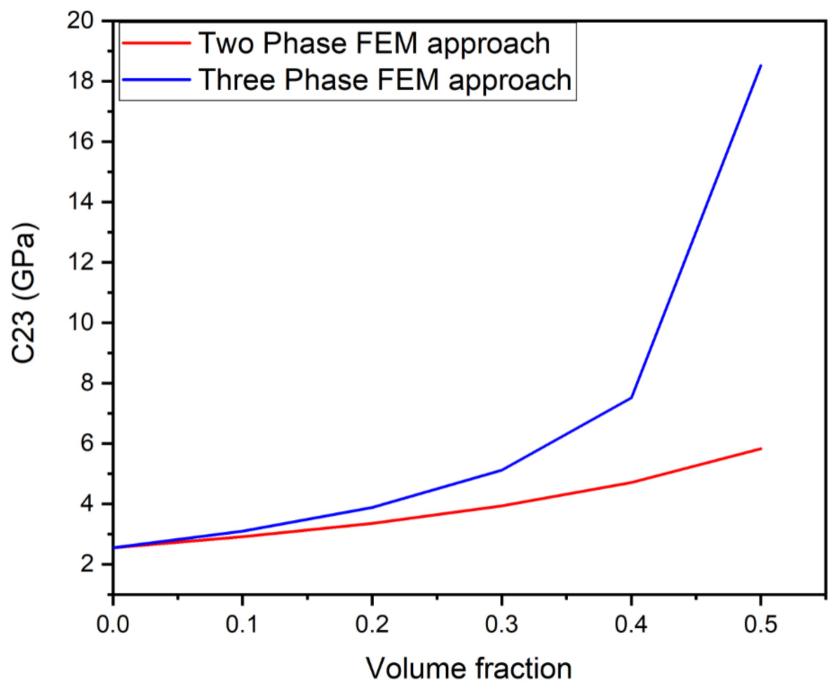

Figure 16 Variation of the effective elastic coefficient C23 of composites against MWCNTs volume fraction.

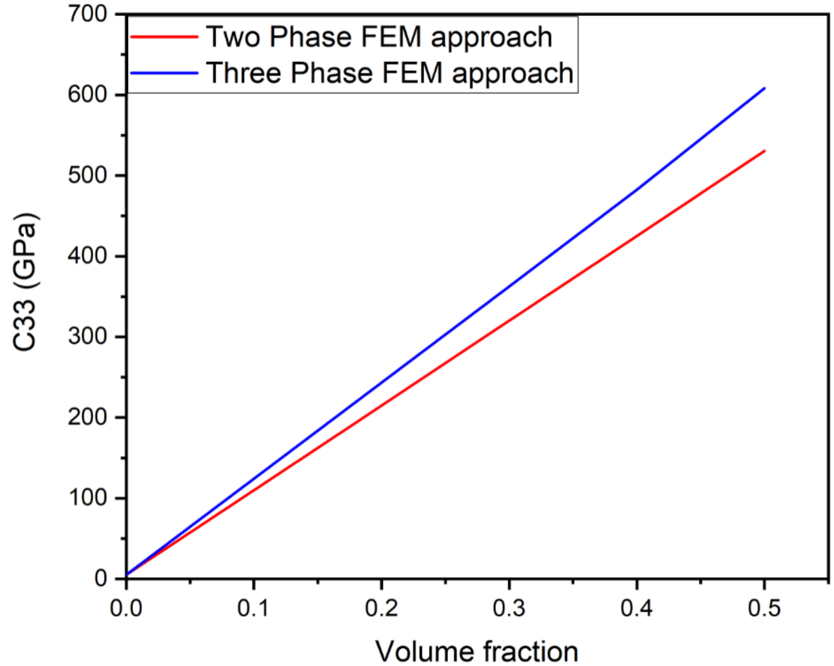

Figure 17 Variation of the effective elastic coefficient C33 of composites against MWCNTs volume fraction.

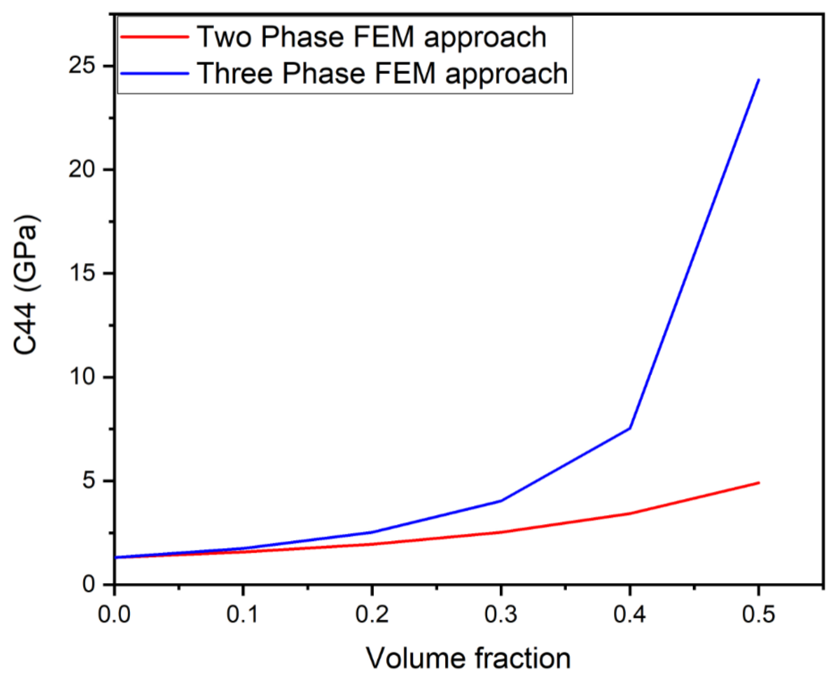

Figure 18 Variation of the effective elastic coefficient C44 of composites against MWCNTs volume fraction.

The following results can be inferred from the above plotted graphs :

1. The addition of CNTs in the epoxy matrix results in an increase in the elastic properties of epoxy in the axial as well as transverse directions as expected for both two-phase and three-phase materials. The elastic properties increase with the increase of CNT content.

2. It is observed that the addition of ZrO_2 as interphase material increases the interfacial bonding between the fiber and the matrix. Thus, a higher increase is observed in the case of three-phase composites as compared to two-phase composite for the same volume fraction of CNT.

4.1.2 Nano scale RVE

A nano scale RVE was modelled which took the small diameter of CNTs in consideration. The dynamic explicit model gives the fracture value of the composite as well as the Young's modulus.

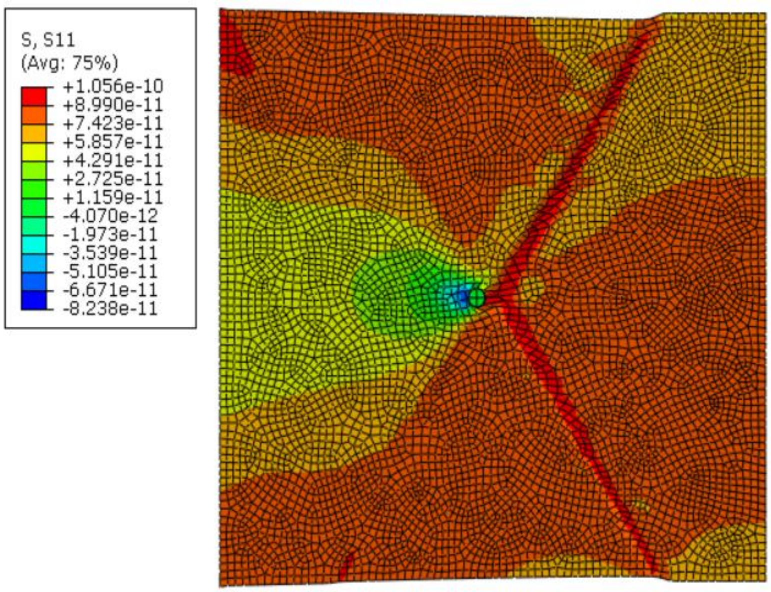

Figure 19 Fractured RVE in dynamic explicit model

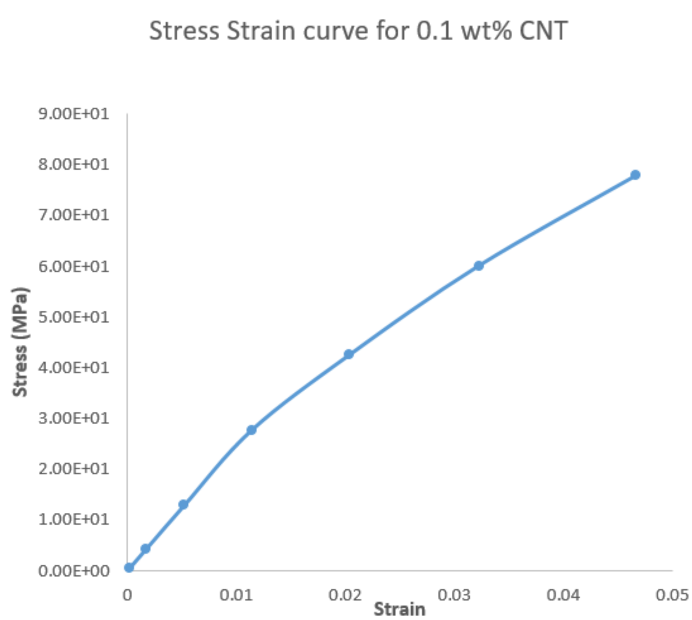

Figure 20 Stress-Strain curve of the nano scale RVE

The Young's modulus of the 1 wt. % MWCNT-epoxy composite is calculated using the linear portion of the curve and is reported to be 2.43 GPa. This result closely resembles the result obtained through experimental procedure by Zhou *et al.* (2007) [33].

4.2 Experimental Results

4.2.1 Tensile Tests

The tensile tests were performed on the specimen of pure epoxy, 0.25 wt. %, 0.5 wt. % and 1 wt. % MWCNT-epoxy specimen using the ASTM D-638 standard on a Universal Testing Machine. The plot shown in *Figure 21* displays the variation in tensile strength with the weight fraction of CNT added.

The following can be inferred from the graph obtained on performing the tensile tests:

1. The ultimate tensile strength of epoxy increased on addition of CNTs up to 0.5 wt. % and then decreased at 1 wt. %.
2. Due to the increase in ultimate tensile strength the composite with improved properties can be used as an important structural material in various applications.

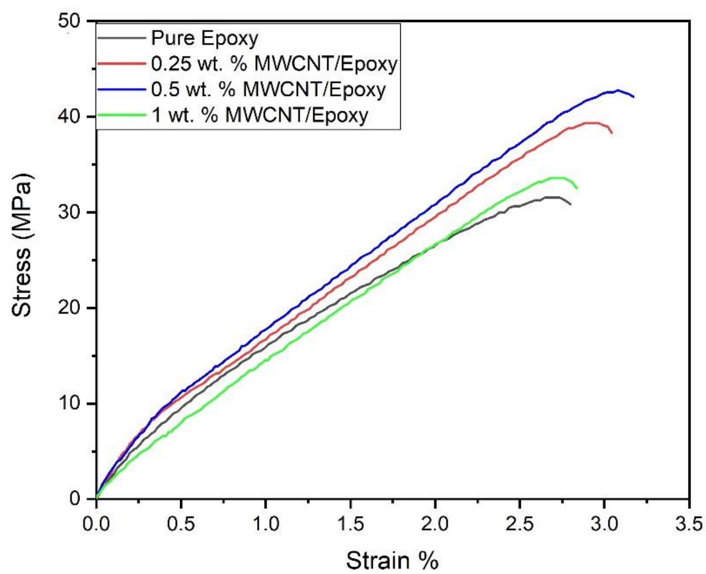

Figure 21 Stress-strain curve from the tensile test

4.2.2 Lap Shear Strength Test

The tensile tests were performed on the specimen of pure epoxy, 0.25 wt. %, 0.5 wt. % and 1 wt. % MWCNT-epoxy specimen using the ASTM D-638 standard on a Universal Testing Machine. The plot shown in *Figure 22* displays the variation in tensile strength with the weight fraction of CNT added.

The following can be inferred from the graph obtained on performing the tensile tests:

1. The average lap shear strength increased on addition of CNTs up to 0.5 wt. % and then decreased at 1 wt. %.
2. MWCNT-epoxy composites can be used as adhesives as they show significant improvements in shear strength.

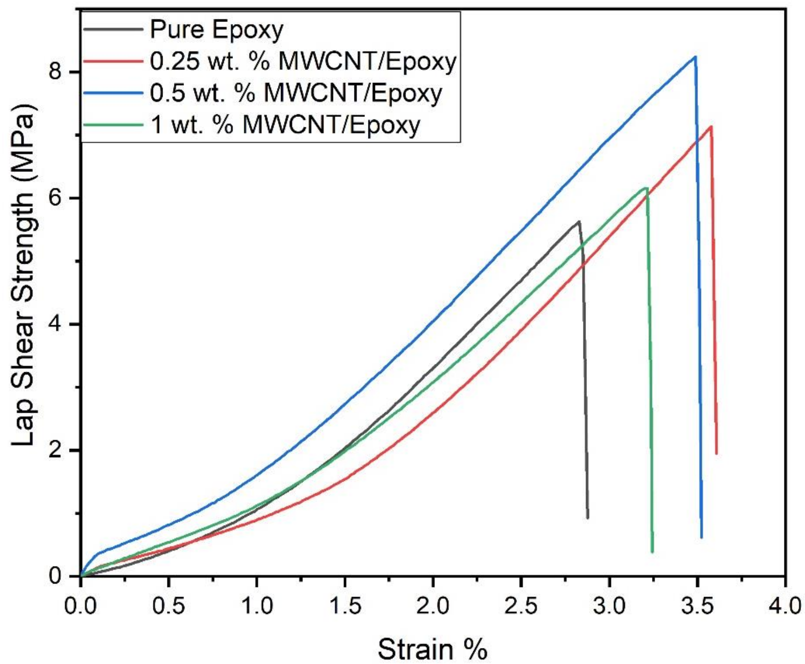

Figure 22 Stress-strain curve obtained from lap shear strength tests

4.3 Discussions

1. The tensile strength and lap shear strength increase significantly on addition of MWCNT upto 0.5 wt % and decrease at 1wt. %. The drop in the value of the ultimate tensile strength and the lap shear strength at 1 wt. %, can be attributed to the agglomeration of the CNTs at higher weight fraction.
2. The agglomeration of CNTs at higher weight fraction results in the reduction of the apparent weight fraction of CNTs. Vacancies are created and load transfer from the matrix to the fibers is hindered which results in an overall decrease in the strength of the composite.
3. The agglomeration of CNTs at higher weight fractions also results in poor interfacial bonding between the fiber and the matrix which might lead to slipping inside the composite and be responsible for the decrease in the strength.
4. Ultrasonic dual mode mixing is an efficient way to homogeneously disperse cluster free MWCNT in epoxy for lower weight fractions of MWCNT (<1wt. %).

Chapter 5

Scope for future work

The current work was has shown that the strength of epoxy can be increased by adding MWCNTs to it. The current work thus has considerable scope for future work some of which can be as mentioned below:

1. The three-phase model showed better results for same weight fraction of CNT as compared to the two-phase model. The current can hence be extended to three phase composites with ZrO_2 as an interphase material and then charactering the mechanical properties of the composite.
2. Various other tests can be performed such as micro-hardness test, three-point bend test, dynamic mechanic analyzer (DMA) test, thermos-gravimetric analysis (TGA) etc. to further characterize the mechanical as well as thermal properties of the MWCNT-epoxy nanocomposite.
3. The parameters of the UDMM process can be altered to study the effect of the parameters in the homogeneous dispersion of the CNTs in epoxy and their impact in the strengths of the nanocomposite.

References

[1] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56e58, http://dx.doi.org/10.1038/354056a0.

[2] Ates, M., Eker, A. A. and Eker, B. (2017) ‘Carbon nanotube-based nanocomposites and their applications’, Journal of Adhesion Science and Technology. Taylor & Francis, 31(18), pp. 1977–1997. doi: 10.1080/01694243.2017.1295625.

[3] Thostenson, E. T., Ren, Z. and Chou, T. (2001) ‘Advances in the science and technology of carbon nanotubes and their composites : a review’, 61, pp. 1899–1912.

[4] Lau, K. and Hui, D. (2002) ‘The revolutionary creation of new advanced materialsĐcarbon nanotube composites’, 33.

[5] Goyat, M. S., Ray, S. and Ghosh, P. K. (2011) ‘Innovative application of ultrasonic mixing to produce homogeneously mixed nanoparticulate-epoxy composite of improved physical properties’, Composites Part A: Applied Science and Manufacturing. Elsevier Ltd, 42(10), pp. 1421–1431. doi: 10.1016/j.compositesa.2011.06.006.

[6] Kumar, K., Kumar, A. and Ghosh, P. K. (2018) ‘UDM enhanced physical and mechanical properties through the formation of nanocavities in an epoxy matrix’, Ultrasonics Sonochemistry, 40, pp. 784–790. doi: 10.1016/j.ultsonch.2017.08.016.

[7] Halder, S., Ghosh, P. K. and Goyat, M. S. (2012) ‘Influence of ultrasonic dual mode mixing on morphology and mechanical properties of ZrO2-epoxy nanocomposite’, High Performance Polymers, 24(4), pp. 331–341. doi: 10.1177/0954008312440714.

[8] Kumar, A. et al. (2018) ‘MWCNTs toward superior strength of epoxy adhesive joint on mild steel adherent’, Composites Part B: Engineering. Elsevier, 143(May 2017), pp. 207–216. doi: 10.1016/j.compositesb.2018.01.016.

[9] Ezekowitz RA, Williams DJ, Koziel H, Armstrong MY, Warner A, Richards FF, R. R. (1991) ‘© 19 9 1 Nature Publishing Group 그라첼꺼’, *Nature*.

[10] Unknown - Unknown - Treacy, Ebbesen, Gibson - 1996 - Exceptionally high Young’s modulus observed for individual carbon nanotubes.pdf.pdf’ (no date).

[11] Lu, J. P. (1997) ‘Elastic Properties of Carbon Nanotubes and Nanoropes’, pp. 1297–1300.

[12] Popov, V. N., Doren, V. E. Van and Balkanski, M. (2020) ‘Elastic properties of crystals of single-walled carbon nanotubes’, 114(2000), pp. 395–399.

[13] Chang, T. and Gao, H. (2003) ‘Size-dependent elastic properties of a single-walled carbon nanotube via a molecular mechanics model’, 51, pp. 1059–1074. doi: 10.1016/S0022-5096(03)00006-1.

[14] Shen, L. and Li, J. (2004) ‘Transversely isotropic elastic properties of single-walled carbon nanotubes’, pp. 1–10. doi: 10.1103/PhysRevB.69.045414.

[15] Liu, J. Z. *et al.* (2005) ‘Mechanical properties of single-walled carbon nanotube bundles as bulk materials’, 53, pp. 123–142. doi: 10.1016/j.jmps.2004.06.008.

[16] Suzuki, K., & Nomura, S. (2007). On Elastic Properties of Single-walled Carbon Nanotubes as Composite Reinforcing Fillers. Journal of Composite Materials, 41(9), 1123–1135. doi.org/10.1177/0021998306067298.

[17] Montazeri, A. *et al.* (2010) ‘The effect of curing cycle on the mechanical properties of MWNT/Epoxy nanocomposite’, *International Journal of Polymer Analysis and Characterization*, 15(3), pp. 182–190. doi: 10.1080/10236661003671744.

[18] Thostenson, E. T. and Chou, T. (2003) ‘On the elastic properties of carbon nanotube-based composites : modelling and characterization’, 573.

[19] Odegard, G. M., Frankland, S. J. V and Gates, T. S. (2003) ‘AIAA 2003-1701 THE EFFECT OF CHEMICAL FUNCTIONALIZATION ON MECHANICAL PROPERTIES OF NANOTUBE / POLYMER COMPOSITES American Institute of Aeronautics and Astronautics American Institute of Aeronautics and Astronautics’, (April), pp. 1–14.

[20] Chen, X. L. and Liu, Y. J. (2004) ‘Square representative volume elements for evaluating the effective material properties of carbon nanotube-based composites’, 29, pp. 1–11. doi: 10.1016/S0927-

0256(03)00090-9.

[21] Seidel, G. D. and Lagoudas, D. C. (2006) 'Micromechanical analysis of the effective elastic properties of carbon nanotube reinforced composites', 38, pp. 884–907. doi: 10.1016/j.mechmat.2005.06.029.

[22] Han, Y. and Elliott, J. (2007) 'Molecular dynamics simulations of the elastic properties of polymer / carbon nanotube composites', 39, pp. 315–323. doi: 10.1016/j.commatsci.2006.06.011.

[23] Tsai, J., Tzeng, S. and Chiu, Y. (2010) 'Composites : Part B Characterizing elastic properties of carbon nanotubes / polyimide nanocomposites using multi-scale simulation', *Composites Part B*. Elsevier Ltd, 41(1), pp. 106–115. doi:10.1016/j.compositesb.2009.06.003.

[24] Pilli, S. C. and Lu, Y. C. (2013) 'Modeling the effective elastic properties of nanocomposites with circular straight CNT fibers reinforced in the epoxy matrix', pp. 3160–3172. doi: 10.1007/s10853-012-7093-8.

[25] Wernik, J. M. and Meguid, S. A. (2014) 'International Journal of Solids and Structures Multiscale micromechanical modeling of the constitutive response of carbon nanotube-reinforced structural adhesives', *International Journal of Solids and Structures*. Elsevier Ltd, 51(14), pp. 2575–2589. doi: 10.1016/j.ijsolstr.2014.03.009.

[26] Alian, A. R., Kundalwal, S. I. and Meguid, S. A. (2015) 'Multiscale modeling of carbon nanotube epoxy composites', *Polymer*. Elsevier Ltd, 70, pp. 149–160. doi: 10.1016/j.polymer.2015.06.004.

[27] Arash, B., Park, H. S. and Rabczuk, T. (2015) 'Mechanical properties of carbon nanotube reinforced polymer nanocomposites : A coarse-grained model', *Composites Part B*. Elsevier Ltd, 80, pp. 92–100. doi: 10.1016/j.compositesb.2015.05.038.

[28] Gupta, A. K. and Harsha, S. P. (2016) 'Analysis of mechanical properties of carbon nanotube reinforced polymer composites using multi-scale fi nite element modeling approach', *Composites Part B*. Elsevier Ltd, 95, pp. 172–178. doi: 10.1016/j.compositesb.2016.04.005.

[29] Powar, B. M. and Shirsat, R. K. (2017) 'Finite Element Analysis of Carbon Nanotube Based

Composites', 7(10).

[30] Hassanzadeh-aghdam, M. K., Ansari, R. and Darvizeh, A. (2018) 'International Journal of Engineering Science Micromechanical analysis of carbon nanotub e-coate d fiber-reinforced hybrid composites'. Elsevier Ltd, 130, pp. 215–229. doi: 10.1016/j.ijengsci.2018.06.001.

[31] Hsiao, K.-T., Alms, J. and Advani, S. G. (2003) 'Use of epoxy / multiwalled carbon nanotubes as adhesives to join graphite', *Nanotechnology*, 14, pp. 791–793. Available at: http://iopscience.iop.org/article/10.1088/0957-4484/14/7/316/pdf.

[32] Song, Y. S. and Youn, J. R. (2005) 'Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites', *Carbon*, 43(7), pp. 1378–1385. doi: 10.1016/j.carbon.2005.01.007.

[33] Zhou, Y. *et al.* (2007) 'Experimental study on the thermal and mechanical properties of multi-walled carbon nanotube-reinforced epoxy', *Materials Science and Engineering A*, 452–453, pp. 657–664. doi: 10.1016/j.msea.2006.11.066.

[34] Halder, S., Ghosh, P. K. and Goyat, M. S. (2012) 'Influence of ultrasonic dual mode mixing on morphology and mechanical properties of ZrO2-epoxy nanocomposite', *High Performance Polymers*, 24(4), pp. 331–341. doi: 10.1177/0954008312440714.

[35] Haldera, S. *et al.* (2013) 'Ultrasonic dual mode mixing and its effect on tensile properties of SiO2-epoxy nanocomposite', *Journal of Adhesion Science and Technology*, 27(2), pp. 111–124. doi: 10.1080/01694243.2012.701510.

[36] Ghosh, P. K., Kumar, A. and Kumar, K. (2015) 'Improving thermal and electrical properties of graphene–PMMA nanocomposite', *Polymer Science - Series A*, 57(6), pp. 829–835. doi: 10.1134/S0965545X15070044.

[37] Kumar, A. *et al.* (2017) 'Thermo-mechanical and anti-corrosive properties of MWCNT/epoxy nanocomposite fabricated by innovative dispersion technique', *Composites Part B: Engineering*. Elsevier Ltd, 113, pp. 291–299. doi: 10.1016/j.compositesb.2017.01.046.

[38] Kumar, A., Kumar, K., Ghosh, P. K. and Yadav, K. L. (2018) 'MWCNT/TiO2 hybrid nano filler toward high-performance epoxy composite', *Ultrasonics Sonochemistry*, 41(May 2017), pp. 37–46. doi: 10.1016/j.ultsonch.2017.09.005.

[39] Kumar, A., Kumar, K., Ghosh, P. K., Rathi, A., *et al.* (2018) 'MWCNTs toward superior strength of epoxy adhesive joint on mild steel adherent', *Composites Part B: Engineering*. Elsevier Ltd, 143, pp. 207–216. doi: 10.1016/j.compositesb.2018.01.016.

[40] Goyat, M. S. *et al.* (2019) 'Superior thermomechanical and wetting properties of ultrasonic dual mode mixing assisted epoxy-CNT nanocomposites', *High Performance Polymers*, 31(1), pp. 32–42. doi: 10.1177/0954008317749021.