# MECHANICAL, ELECTRICAL AND EMI SHIELDING RESPONSE OF MWCNT/EPOXY NANOCOMPOSITES

**M.Tech.** Thesis

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# DISCIPLINE OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020

# MECHANICAL, ELECTRICAL AND EMI SHIELDING RESPONSE OF MWCNT/EPOXY NANOCOMPOSITES

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Technology

With specialization in Mechanical Systems Design

*by* **Pavan Shahapurkar** 



DISCIPLINE OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020



## INDIAN INSTITUTE OF TECHNOLOGY INDORE

## **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **MECHANICAL, ELECTRICAL AND EMI SHIELDING RESPONSE OF MWCNT/EPOXY NANOCOMPOSITES** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DISCIPLINE OF MECHANICAL ENGINEERING, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from *May 2019* to *June 2020* under the supervision of **Dr. Shailesh I. Kundalwal**, Associate Professor, Dept. of Mechanical Engineering, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Pavan Shahapurkar

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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## Abstract

The remarkable properties of multiwalled carbon nanotubes (MWCNTs) have sparked much attention in recent years. MWCNT shows extraordinary mechanical, electrical and EMI shielding properties. Therefore, they are widely used in automobile, aerospace and electronics industries. The dispersion of MWCNTs in epoxy matrix enhanced the mechanical strength and toughness of MWCNT/epoxy nanocomposites. However, uniform dispersion and good interfacial interaction of MWCNTs with epoxy matrix is the key issue for preparation of high strength polymer nanocomposites. Therefore, in this work, we use ultrasonic mixing technique for homogenous dispersion of MWCNTs into epoxy matrix to produce high strength polymer nanocomposites. Further, the mechanical characterization has been done by performing tensile strength test and lap shear strength test. The viscoelastic behavior of MWCNT/epoxy nanocomposites were studied by performing Dynamic Mechanical Analysis test. Results revealed that the homogenous dispersion of MWCNTs in epoxy matrix enhanced the tensile strength, toughness, lap shear strength and storage modulus of MWCNT/epoxy nanocomposites.

However, adding MWCNT to epoxy matrix not only enhanced the mechanical properties but also its electrical properties, which lead to its use for electronic applications like EMI shielding, supercapacitor electrodes etc. In this work, the electromagnetic interference (EMI) shielding effectiveness (SE) of CNT-epoxy nanocomposites were studied analytically by considering the tunneling effect of carbon nanotubes (CNT) in epoxy matrix. The shielding effectiveness was reported as a function of weight percentage of CNTs and thickness of CNT-epoxy nanocomposites. The tunneling conductivity of CNT-epoxy nanocomposites was measured by considering different parameters such as aspect ratio, interphase thickness and waviness of CNT and their effect with simultaneously change in weight percentage (wt. %) of CNTs. These results concluded that the best conductivity was obtained with MWCNT having a high aspect ratio, thick interphase thickness and small waviness. Moreover, the variation of this conductivity was also simulated to estimate shielding effectiveness of CNT-epoxy nanocomposites. This reflects that a good shielding effectiveness was obtained at a higher concentration of CNT with thicker nanocomposites.

It becomes important to know the minimum amount of MWCNT required to achieve the desired EMI shielding effectiveness, as higher MWCNT filler content, after some particular MWCNT content, decreases its strength. Also, determining the electrical conductivity and EMI shielding effectiveness of the nanocomposite experimentally by varying weight percentage, specimen thickness and aspect ratio of CNTs will be time consuming and loss of material, efforts and capital. Hence, we need to analytically model the electrical conductivity and SE of the nanocomposite considering all these critical factors. Later, depending on the required EMI S.E and electrical conductivity, we can control the critical factors to achieve the required characteristics of the nanocomposite.

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# Chapter 1 Introduction

#### **1.1 Background research**

Use of wireless technology in day to day life has necessitated the need of proper functioning of wireless devices operating in the same environment. Electromagnetic radiations radiated from numerous devices hampers the normal operation of electronic devices and systems producing electromagnetic interference (EMI) [1]. The electromagnetic interference (EMI) is basically electrical in nature and is due to unwanted electromagnetic emission being either conducted or radiated. The issues of tackling electromagnetic compatibility are challenging and proper EMI shielding mechanism has to be ascertained. The EMI shielding can be achieved either by reflection or absorption of the interfering electromagnetic wave [2]. Metals are considered to be the best materials for reflection electromagnetic shielding but the reflected wave may interfere with the electronic component inside the enclosure or in its vicinity. Modern warfare where radar system of weapons detection and guiding missiles are needed; hiding radar signatures and camouflaging war equipment are also important issues to be considered [3]. EMI shielding through absorption mechanism, works on the principle of absorption of the interfering electromagnetic wave by converting the wave energy into thermal energy, thereby reducing the interference to a sufficiently low value [4]. However, shielding by absorption requires certain design conditions while developing the absorber and this shielding mechanism is frequency dependent. Absorbers used for shielding in microwave or radio frequency range are termed as microwave absorbing material (MAM) or radar absorbing material (RAM). The RAM also finds applications as coating on the surface of the military aircraft to avoid detection, in radio frequency anechoic chamber, in food processing technology etc. [5-8]. Generally, RAMs are prepared in the form of sheets comprising of insulating polymer (rubber, magnetic or dielectric loss materials).

When electromagnetic wave emitted from one of the devices interferes with the normal operation of another device, such a condition is referred as electromagnetic interference. Effects of electromagnetic interference can be observed in day to day life. Some of the common examples are listed here

- Temporary disruption in the operation of television and reception of radio signals owing to the use of mixer grinders, trimmers, vehicles passing by the road etc.
- Flight control system malfunctioning attributed to the use of laptop and electronic devices by the commuters.
- Severe disturbances in the working of pace maker employed in a patient due to the operation of walkie-talkie.
- It can lead to change of setting of status of control equipment and reset the computers leading to loss of data.
- Environment & living systems are also affected.

Thus, apart from disturbing the proper functioning of electronic devices, it may also result into loss of income, time and energy and also serve as threat to the living beings in the form of environmental pollution. There is a rapid rise in the electromagnetic noise owing to the excessive use of electronic devices. Exposure to such noise severely affects the human body. The most of transmitted electromagnetic radiations get absorbed by the human body causing disorders like skin rashes, muscle soreness and so on. The advancements in the electronic industry and tremendous urge for use of electronic devices in various applications; and as technology evolves to make devices lighter, faster and smaller, the problem of electromagnetic interference (EMI) have magnified and become severe. With the advances of wireless electronic devices, the electromagnetic radiations have covered the entire environment and are now are posing a serious threat. Due to escalating EMI issues, the attention of scientific community has gone to develop materials and methods as a blocking mechanism to control it. Interference in electronic circuits is primarily due to the transmission coupling of electromagnetic signals and can be avoided by using proper circuit design and frequency filters. Further, radiation can be avoided by segregating the source with a physical shield. Thereby EMI shielding is used to mitigate electromagnetic radiation from emitters with the materials capable to interrelate with the signals. Shields can incapacitate an incident wave to enter into a certain space by absorption-dissipation and/or reflection [9]. Usually, conductive metallic panels and meshes are utilized for insulating spaces by reflecting the incident radiation. Faraday cages are related with the theory of pure reflection shielding wherein the inner space is made completely isolated to exterior electric fields. Alternatively, shielding by absorption is usually related to materials that are magnetically permeable like ferro and ferrimagnetic materials. Propagation of incident magnetic field into other spaces is prevented by the use of magnetic absorbers. However, for metallic conductors, high density and processing cost coupled with lack of flexibility hinder their use. Additionally, the inherent cut-off frequency of ferro and ferrimagnetic materials is normally lower than the low-GHz range confining their use in GHz-shielding based applications. Presently more emphasis is given to find broadband shields that have the ability to nullify electromagnetic radiation up to GHz range. There is an ever increase in consciousness towards electromagnetic pollution and adverse effects caused due to the use of high frequency devices [10]. The concern of pollution caused due to electromagnetic interference not only affects consumer appliances but also affects heavy industries. The aforementioned sectors and devices require effective shielding materials against electromagnetic interference that meet the specified pre-requisites of design criteria.

#### **1.2 Epoxy as matrix**

Polymers are long chain organic molecules or macromolecules with many desirable properties such as high ductility, ease of forming and noncorrosiveness [11]. A wide variety of such materials are available to a designer. Two such classes are thermosetting and thermoplastic polymers. Their initial target applications were in aerospace and later became viable alternative material in the sporting, automotive and in construction industries. In thermosetting polymers, there are covalent cross bonds (cross link) between molecules, in addition to Van der Waals forces. Owing to these cross bonds, a thermosetting polymer remains rigid on heating [12]. Thermoplastic polymers can be re-shaped by repeated heating and cooling without losing their properties [12]. They soften on heating and become rigid on cooling. On the other hand, thermosets remain rigid during reheating till they are converted into char. This difference in behavior on heating is due to the relatively weak Van der Waals forces acting between the molecules of thermoplastic polymers. On heating, the bonds between the molecules weaken substantially and the material becomes soft and yieldable.

Thermosetting epoxy resin being one of the most habitually used polymeric matrix material for composites, is widely available in a range of varieties from high melting solids to low viscosity liquids and can be modified quite susceptible to a range of processes and modifications. They offer good adhesion and soaking of surfaces, high strength, exceptional electrical insulation and less shrinkage along with ease of curing by a variety of chemical agents which make them ideal to be used in composites. Cross linking of epoxide groups (two carbon atoms and one oxygen) takes place in epoxy resins. By adding chemical agents, curing of epoxy resins can be done to make an inflexible molecular structure which will be helpful to use them at elevated temperatures. Primarily, epoxies are employed for composite applications in the following classes – aromatic glycidyl amines, cycloaliphatics and phenolic glycidyl ethers. A type of phenolic glycidyl ether, diglycidyl ether of bisphenol A (DGEBA) is the most commonly used epoxy. Anhydrides, amines or amine derivatives are some important curing agents used in epoxy resins as hardeners. Even modifiers can be utilized to vary the mechanical and physical functionality of cured or uncured resins, which include thermoplastics, rubbers, flame retardants, pigments and fillers.

The epoxy resin possesses high strength, good resistance to various chemicals and environments, easy to process and are low-cost materials. Furthermore, epoxy as adhesives are suitable to bond with various types of substrates such as metal, plastic, rubber, glass, ceramic and wood [13]. They can easily fill gaps and provide excellent sealing properties against various chemicals [14]. In spite of several merits of epoxy as mentioned above, they possess some serious disadvantages like their brittleness, which restricts their applications in advanced structure due to safety reasons. The epoxy resin has low toughness and poor resistance to crack propagation. To overcome these problems, various types of nanofillers have been tried out by the researchers around the world. The major challenges of epoxy resins are that the cured epoxy

resins are brittle polymers and have low fracture toughness, poor wear behaviour and low fracture energy.

#### 1.3 Carbon nanotubes as a nanofiller

The Carbon nanotube (CNT) is an allotrope of carbon, which was discovered by Iijima (Iijima, 1991) in NEC laboratory of Japan during fullerene synthesis. Carbon nanotubes (CNTs) have cylindrical nanostructure of predominantly hexagonal of carbon atoms with large length upto several microns and small diameter in nanometers range, which result in large aspect ratio. Therefore, CNTs are expected to possess unusual thermal, electrical and mechanical properties, which generate much potential application in the field of conductive and high-strength nanocomposite, hydrogen storage media, nanometer-sized semiconductor devices, EMI shielding, energy conversion devices, sensors, probes and interconnect [15,16]. CNTs can be categorized into Single Walled Carbon Nanotubes (SWCNTs) (Fig. 1.2) and Multi Walled Carbon Nanotubes (MWCNTs) (Fig. 1.2). For SWCNTs, it is thought-about to be formed by rolling of a single layer of graphene into a faultless cylinder. Similarly, MWCNTs are nothing but coaxial assembly of multiple SWCNT cylinders, one within another, and these concentric tubes are held together by weak van der waals forces.



Figure 1.1 Schematic Structure of (a) Single Walled Carbon Nanotubes (SWCNTs) and (b) Multi Walled Carbon Nanotubes (MWCNTs) [AZoNano (2004), AZoNano(2013)]

CNTs have extremely high mechanical, thermal, electrical and magnetic properties, high stiffness, thermal conductivity and low density. CNTs are high

strength materials examined in terms of tensile strength and elastic modulus, which may be due to the formation of covalent sp2 bonds formed between the individual carbon atoms. Carbon nanotubes have low thermal conductivity in transverse direction but high thermal conductivity in its axial direction. Studies says that CNTs have high thermal conductivity i.e. 6000 W/mk at room temperature [17]. CNTs can act as a metal like conductor or semiconductor, depending on their diameters and helical arrangement or chiral angle. CNTs are highly flexibility and can be bend without breaking. CNT have high aspect ratio and high field emission. Because of the above-mentioned properties, CNTs are widely used as reinforcing agent with polymers for studying various properties. CNTs act as an ideal nanofiller material, and have been used as reinforcing agent with polymers for studying various properties.

Carbon nanotubes are small but high aspect ratio conductive nanofillers which can be used for all types of plastics. The high aspect ratio means, to attain the same electrical conductivity, a lower filler loading of CNTs is required in comparison to the other available conductive nanofillers, which helps in preserving most of the key performance characteristics of polymer resin, mainly its toughness at low temperatures. For electrical conductivity in plastics, CNT nanofillers have proven to be an ideal additive. When compared to traditional additives like chopped carbon fiber, stainless steel fiber, or carbon black, electrical conductivity is imparted even at lower CNT filler loading due to its high aspect ratio (about 1000:1). [18]

#### 1.4 Methods used for preparation of polymer nanocomposites

#### 1.4.1 Direct mixing

Direct Melt mixing is the most common method for preparation of nanocomposites. In this process, extruders or injectors equipment's are used for synthesis of polymer nanocomposites. For example, a high velocity oxy-fuel (HVOF) combustion spray process has been successfully applied for the preparation of silica filled nylon composites.

Melt mixing method has certain disadvantages. This method does not form a strong interaction force between the polymer matrix and nano scale filler. Nanoscale fillers used in polymer composites have strong ability to aggregate together and form clusters. So, for this, surface modification of nanofiller or nanopowders is required. Another drawback of this process is the rapid rate of viscosity by the addition of small volume fraction of nanopowders.

#### 1.4.2 Sol-Gel Processing

The Sol-Gel Method was used for the preparation of hybrid polymers in 1980 [19]. By this technique, the inorganic-organic hybrid polymer composites were prepared by addition of organic-inorganic nanofiller with the polymer matrix which cause the polymer solubility and compatibility of the solvent. Wu and Liao were the first who purposed the sol gel processing technique [20]. This is a slow processing technique.

#### **1.4.3 In Situ Intercalative Polymerization**

In the past, this methodology has been conspicuously used for preparing polymer/layered silicates nanocomposites. Before undergoing polymerization, layers of clay are dispersed in the monomer solution. Swelling of silicate sheets takes place in a monomer solution, ensuing to achieve a polymer in the interlayer house of silicate layers after monomer undergoes polymerization. Due to heat or radiation, polymerization takes place. However, it may also take place due to diffusion of an acceptable initiator or catalyst by cation exchange within the inter gallery house followed by the swelling step. But when we discuss about dispersion of nanofiller in polymer matrix, ultrasonication mixing is the best technique for polymer nanocomposites synthesis [21].

#### 1.4.4 Ultrasonication mixing process

In some recent works, it is reported that the newly developed technique where ultrasonic vibration along with axial flow impellor used for polymer nanocomposite preparation is capable of modifying epoxy structure arrangement and to achieve better homogeneous distribution of nanofillers in semi-viscous matrix. The properties of a nanocomposite are immensely dependent on interfacial area between polymer and the nanofillers. Degree of curing, crystallinity and the polymer chain mobility are affected by the chemical properties of this region. There are some processing methods to control the size of the interfacial zone and dispersion of nanofillers. Reducing the surface energy and hence dispersing the nanofillers in the matrix can be achieved by some preprocessing methods. Ultrasonication brings about alternating high-pressure and low-pressure waves in nanocomposite solution, which leads to the formation and bursting of small vacuum bubbles. This phenomenon is called as cavitation which induces strong hydrodynamic shear-forces and high-speed impinging liquid jets. These effects are used to deagglomerate the nanofillers in polymer matrix. In this aspect, ultrasonication is an alternative to high-speed mixers and agitator bead mills. Hence, ultrasonication has been used as a method of dispersing nanofillers in numerous matrices [22].

#### **1.5 Problem for Preparation of Polymer Nanocomposites**

The properties of polymer nanocomposites can be improved by achieving good bonding between CNTs and the matrix. Hence, in order to achieve the desired nanocomposite properties, dispersing the CNTs as individual particles in the epoxy matrix is the biggest challenge. Until now, in-house synthetized CNTs and commercially available CNT powders comprise of agglomerates where the CNTs stick strongly together due to adhesive forces. Moreover, adhesive forces add up with decreasing particle size and increasing SSA. A poor dispersion of CNTs degrades their reinforcing potency in the epoxy matrix, caused by the CNTs slipping by one another once forces are applied, however conjointly ends up in the micro-voids' formation in the nanocomposites [23]. Hence, the method used to disperse the CNTs as separated individual particles in epoxy is considered to be of prime importance during nanocomposite processing stages. High shear mixing and ultrasonication are the two main methods to disperse nanoparticles in epoxy resin effectively. Ultrasonication techniques, both tip and bath sonication, are capable of combining the particle agglomerates breakage with an effective mixing of the epoxy and additives at a Ultrasonication can be applied directly molecular level. to the epoxy/nanoparticles mixture, however the common practice is to use of solvents to decrease the viscosity of the system. The employment of surfactants and solvents has also been helpful to disentangle CNT agglomerates effectively in some cases. However, high intensity and long length ultrasonication treatments

may cause localized damage and shortening of the CNPs [24]. Moreover, eviction of the solvents turns out to be an important step during the processing of nanocomposites because any trace of solvent in the final material can significantly have an effect on its properties. On the other hand, the dispersion of CNTs throughout the matrix volume is very low because as the distance from the tip increases, the vibrational energy decreases. For these reasons, sonication has also been used together with mechanical stirring or other high shear forces methods [25-27].

#### **1.6 Electrical Conductivity**

There are different analytical models to evaluate the effective electrical conductivity of composites in general. Most of them are based on critical volume fraction called as percolation threshold.

#### **Percolation threshold:**

In composites, the overall electrical conductivity is largely characterized ٠ by its dependency on the filler loading content. The electrical conductivity of the composite stays close to the low conductivity of the pure polymer matrix at lower filler loadings. Further when the filler loading is increased and it reaches a critical value, known as the percolation threshold, the physical phenomenon will increase many orders of magnitude with very little increase in the filler quantity. After this region of drastic increase, the physical phenomenon yet again levels off and is on the brink of that of the filler material. It indicates that sufficient amount of filler has been added such that a continuous conductive network through the nanocomposite has been formed. For electric conduction in composite films, there is no compulsion of fillerfiller direct contact for current to flow; ideally, by tunneling between the polymer layers which envelope the filler particles, the current can flow. In the insulating polymer matrix, when conductive filler loadings are low and uniformly dispersed, the electron transport is controlled by the electron tunneling resistance between the conductive filler junctions.

Percolation threshold helps us to estimate the state of dispersion of different fillers in the polymer matrices qualitatively [28].

Some of the models are discussed below:

#### 1.6.1 Power law

Kirkpatrick [29] proposed a statistical percolation model called as the power law equation which helped in predicting the electrical conductivity of materials. Even though it was effective, the equation did not prove to be as accurate as experimental data [30,28]. Anyhow, when [30] the experiment was conducted on the (copper, nickel)/epoxy resin, and poly(vinyl chloride) with metal mixture, power law model was found to be effective enough; this proposes that the randomly distributed mixture of materials with metal-like structure can be modelled by power law equation.

The assumptions made in this model are noteworthy, electron hopping distance was considered negligible, also the conducting particles ought to be physically in contact with one another to form an electrically conductive network, are some of the assumptions made. However, if electrical percolation is dealt with a simple scaling equation, this law seems to be unreliable when nanoparticles are well distributed in the matrix with very low aggregation problems. Moreover, the equation stands valid only for a small range of filler loading phase right above the percolation threshold. Also, the model is restricted to the cases where either the host matrix has zero conductance or the additive has zero resistance [31].

#### 1.6.2 Model by Fei Deng and Quan-Shui Zheng

The experimental results have revealed that, addition of CNTs have immensely improved the electrical conductivity of the host matrix of the CNT composites. But unlike other basic models, this model considered various critical factors that eventually contribute to the electrical conductivity of the nanocomposite. Along with electrical conductivity, this model considered factors like percolation threshold, CNT conductivity anisotropy, nonstraightness and aspect ratio. The model predictions were in good agreement with the experimental data available in literatures. It was later widened to address the effect of CNT's orientation distribution, but failed to account the tunneling distance between CNTs [32].

#### 1.6.3 Model by Yasser Zare and Kyong Yop Rhee

Unlike other models, this model considers the tunneling distance between the CNTs. It characterizes the main tunneling conductivity of CNT/polymer nanocomposites by considering the CNT waviness, tunneling distance and interphase around CNT. By using an extended CNT (which includes tunneling space and CNT), the role of tunneling distance is considered in this model, whose electrical conductivity is calculated by a simple equation. Also, by using some more simple equations, the effects of the CNT waviness and interphase on the percentages of percolated CNT, effective filler fraction, and percolation threshold are described. The model prediction agrees well with the experimental results. To achieve high desirable conductivity, short tunneling distance, thick interphase, poor percolation threshold, dense network, high concentration of straight, long, thin, and super-conductive CNT filler properties are required [33].

#### **1.7 Shielding Mechanism**

When the electromagnetic wave is made incident on the outer surface of the material three types of interactions take place namely absorption, reflection and transmission as shown in the figure 1. As the wave passes through the material it can either be absorbed, reflected or transmitted through the other end of the material. Total shielding efficiency can be defined by the basic concepts of reflection and transmission.

Ability of a material to obstruct electromagnetic energy of a particular frequency passing through it can be estimated by this parameter. Shielding effectiveness relates the incident electromagnetic energy to the transmitted one. SE is defined as the ratio of incident EM waves entering ( $E_e$ ) and departing ( $E_d$ ) the material and is given by

$$SE = 10 \log_{10} \frac{E_e}{E_d}$$



Figure 1.2 Representative diagram of the possible interactions of electromagnetic wave with composites.

Three primary interactions are observed within the material when an incident EM wave passes through the material, namely, absorption (A), reflection (R) and transmission (T). Reflected wave comprises of reflection from the material surface and multiple reflection occurring within the material. For monolithic isotropic materials, absorption can be calculated by determining the transmittance and reflection and is given by

$$A = 1 - R - T$$

For composite or hollow materials, reflections from the inner surface demonstrate significant drop in the transmitted signal. Such a mechanism cannot be termed as absorption but instead the effective attenuation coefficient ( $\alpha$ ) can be calculated by combining the effect of reflection mechanism with the absorption of the porous material as

$$\alpha = 1 - R - T$$

Schelkunoff's theory reveals that total shielding effectiveness ( $SE_T$ ) of a material is due to absorption, reflection and multiple reflections. Further it states that, if absorption loss is less than 10 dB, the effect of multiple reflections can be neglected and the cumulative shielding effectiveness can be estimated using reflection and absorption losses only.

$$SE_T = SE_A + SE_R$$

#### 1.8 Organization of thesis

The chapter - wise summary of the thesis is given below.

**Chapter 1** presents motivation and background information about the polymer nanocomposites, especially epoxy nanocomposites, and the importance of reinforcing carbon nanotubes in epoxy in order to change its physical, mechanical, electrical and EMI shielding properties. The problems faced during preparation of nanocomposites is also discussed. In the later parts, percolation threshold, various analytical models for electrical conductivity and EMI shielding theory is briefed.

**Chapter 2** presents a literature review on polymer nanocomposites, especially MWCNTs as reinforcing nanofiller and epoxy as a polymer matrix. The research gaps have been identified and objective of present study have been finalized.

**Chapter 3** describes experimental procedure for the preparation of MWCNT/epoxy nanocomposites by application of ultrasonication dual mixing technique with ultrasonicator and an axial flow impellor, for cluster free homogeneous distribution of MWCNTs in matrix. This chapter also discusses the surface treatment of copper substrate for the preparation of nanocomposite adhesive based single lap joints. Tensile and lap shear strength, and viscoelastic properties have been measured using Universal Testing Machine (UTM) and DMA 8000 (Perkin-Elmer) respectively.

**Chapter 4** this chapter represents the results and discussions section of this thesis work. The effect of cluster free homogenous distribution of MWCNT nanofiller reinforced in epoxy matrix, on mechanical properties such as tensile strength, lap shear strength, toughness, and viscoelastic behaviour has been analyzed.

**Chapter 5** The conference paper "Micromechanical analysis of effective elastic properties of graphene reinforced PMMA nanocomposites" submitted at International Conference on Precision, Meso, Micro & Nano Engineering, [COPEN-11], Indore from my current work has been discussed here.

**Chapter 6** "An analytical methodology to evaluate the electromagnetic interference shielding effectiveness of epoxy/CNT nanocomposites in C- band (4-8.2 GHz) by the role of tunneling conductivity of CNTs" from my analytical modelling work will be discussed in this chapter.

Chapter 7 Based on the present study, conclusions and future scope of the research work is discussed in this section.

# Chapter 2 Literature Survey

#### **2.1 Introduction**

In this chapter, a comprehensive literature review on polymer nanocomposites, especially with MWCNTs as reinforcing nanofiller and epoxy as a polymer matrix. This literature review helps us to analyze the different approach used for processing and preparation of polymer composites, along with their application and contents of nanofiller used in it. Finally, preparation, properties and applications of MWCNT/epoxy polymer nanocomposites are also discussed in details.

#### 2.2 Literature review of polymer matrix nanocomposites

**Seong Hun Kim et al. (2003)** showed that the overall EMI shielding effectiveness was dependent on the electrical conductivity of the composites and lied in range of 5–40 dB. High conductivity composites showed reflection-dominant EMI shielding attributes, typical of a metal's EMI shielding attributes. Nevertheless, low conductivity composites displayed absorption-dominant shielding attributes [34].

**Meguid et al. (2004)** investigated the effect of cluster free homogenous dispersion and interfacial interaction of different contents of nanofiller on different properties of polymer matrix. CNTs and alumina powder were used as a nanofiller. An investigation has also been done to study the influence of nanofiller on tensile and shear properties of polymer composites. The results show that the different loading of nanofiller and dispersion of nanofiller significantly enhanced the strength of the interface as well as tensile and shear properties of nanofiller reinforcement with polymer matrix [35].

**Ning Li et al. (2006)** investigated EMI Shielding effectiveness in the 10 MHz to 1.5 GHz frequency range, where the highest value of SE (49 dB) was achieved with 15 wt. % SWCNT at 10 MHz, but the same reduced to 15–20 dB for the 500 MHz to 1.5 GHz frequency range. Also, it was found that, the EMI SE

correlated with DC conductivity and the SE was reflection dominant in this frequency range. The effects of SWCNT aspect ratio and wall defects on the EMI shielding effectiveness were also studied [36].

**Zhou et al. (2006)** investigated different weight percentage of MWCNT/epoxy nanocomposites which were prepared using high intensity ultrasonic liquid processor and high-speed mechanical agitator and their responses for DMA, TGA and flexural tests were recorded. The results showed that strength of the nanocomposites increased with addition of MWCNT up to 0.3 weight percent [37].

**Chatterjee et al. (2008)** investigated the matrix properties by introducing  $TiO_2$  nano fillers into an epoxy resin. For their homogenous mixing, ultrasonic mixing technique was employed for dispersion of  $TiO_2$  particles in epoxy matrix. The incorporation of  $TiO_2$  particles enhanced the thermal, mechanical and viscoelastic properties of polymer composites. The mechanical performance and thermal stability of the epoxy nanocomposites which depend on the good dispersion state of the  $TiO_2$  particles in the epoxy matrix, significantly improved the storage modulus, Tg and other mechanical properties like flexural strength [38].

**Medina et al. (2008)** analysed the effect of  $ZrO_2$  nanoparticles on  $ZrO_2$  nanocomposites prepared by mechanical mixing and dispersing technologies. A detailed study of the mixing parameters has been done for homogenous distribution. The tensile modulus of the epoxy matrix is improved with increase in nano zirconia content. The  $ZrO_2$  nanoparticles increased the KIC and GIC of the epoxy matrix [39].

**Al-Saleh et al. (2009)** analysed the electromagnetic shielding mechanism of MWCNT/PP composites. The results showed that, absorption was the primary shielding process with reflection being secondary one. Also, multiple-internal reflections significantly reduced the overall electromagnetic shielding mechanism. The electromagnetic shielding mechanism of MWCNT/PP polymer composites improved with increasing the wt.% of MWCNT content and thickness of shielding plate [40].

**Ma et al. (2010)** stated that the carbon nanotubes have high strength and high aspect ratio, and provide superior mechanical and thermal properties along with multifunctional characteristics. For carbon nanotubes to be used as an effective reinforcement, appropriate interfacial adhesion between CNTs and polymer as well as uniform dispersion of CNTs is a compulsion. This paper analysed the CNTs effects on different properties of polymer matrix and also evaluated the effects of homogenous dispersion and interfacial interaction of properties of polymer composites [41].

Anh Son Hoang (2011) investigated MWCNT-pure polyurethane resin composite. The measurement of EMI shielding effectiveness was carried out in X-band (8–12 GHz) and results showed that, even with a low MWCNT filler loading, the composites achieved a high conductivity. Also, their EMI shielding effectiveness showed strong dependence on MWCNT concentration. The composite films attained SE of 20 dB for 22 wt.% of MWCNTs [42].

**Montazeri et al. (2011)** described the effect of dispersing medium and sonication time for a 0.1 wt.% MWCNT in MWCNT/epoxy nanocomposite. The results indicated that, at initial stages, tensile strength values increased with increment in sonication time, but in the long run for longer sonication times, the values started decreasing [43].

**Gallego et al. (2013)** compared the filler percolation network of MWCNTs and functionalized graphene sheets (FGSs) in an epoxy resin. He found that, MWCNT readily formed a filler network compared to FGS but the mechanical performance of the cured FGS nanocomposites outperformed the MWCNT [44].

**Rafael Vargas-Bernal et.al** (2013) studied four analytical models to determine conductivity in a CNT-polymer nanocomposite, such that all the reliable design parameters are noted down, which will help to enhance the electrical properties of the composite by means of carbon nanotubes [45].

Fei Deng and Quan-Shui Zheng (2014) showed that along with CNT concentration and percolation threshold, how other factors like CNT conductivity anisotropy, aspect ratio, and non-straightness, affect the overall electrical conductivity of the nanocomposites. The electrical conductivity

predictions made by this model, agreed well with the experimental data available in literatures and the model was later modified to address the effect of CNT's orientation distribution [32].

Halder et al. (2015) investigated the application of Ultrasonic dual mode mixing (UDMM) to analyse the thermo-mechanical behaviour of  $ZrO_2$  particles reinforced epoxy nanocomposite. Different amplitudes i.e 40% and 55%, for ultrasonic dual mixing method were used for synthesis of  $ZrO_2$ -epoxy nanocomposites. The different amplitude of UDMM process helped to analyse the dispersion behaviour of  $ZrO_2$  particles in epoxy. At high amplitude the value of Tg and thermal stability significantly improved. Thermo gravimetric analysis has been employed to study about thermal stability [46].

**Mohammed H. Al-Saleh (2015)** showed that only 0.054 vol% of CNT was required to electrically percolate the CNT/polymer nanocomposite system. Also, EMI SE of 50 dB was reported for a 1.0 mm plate made of 10 wt.% CNT nanocomposites [47].

**Ghosh et al. (2016)** analysed the Lap shear strength of nanocomposite adhesive joint with substrate as mild steel and aluminium. The adhesive strength of the substrate significantly depends upon the bond line thickness of dissimilar joints of mild steel and aluminium. The optimal bond line thickness varied with rolling load of 4.2 N. The chemical treatment of dissimilar metal surface with same rolling load gave better enhancement in lap shear joint strength as compare to the mechanical treated surface of different metal. For this purpose, the incorporation of TiO<sub>2</sub> nano filler significantly helped in improvement of lap shear strength. [48].

**Komeil Nasouri et al. (2016)** investigated EMI shielding response of MWCNT/polyvinylpyrrolidone nanocomposite prepared by electrospinning process, in which MWCNTs were mixed with polyvinylpyrrolidone. The EMI SE and complex permittivity of all nanocomposite were determined in the X band (8.2–12.4 GHz) frequency range. Also, the analytical model for predicting the EMI shielding was a function of the electrical conductivity, permittivity, specimen thickness and frequency [49].
**Kumar et al. (2017)** examined the influence of different contents of MWCNTs on cluster free homogenous dispersion of epoxy-based nanocomposites by using the ultrasonication mixing process followed by axial flow impeller for the polymer nanocomposite preparation. The FESEM analysis has been done to study the dispersion of MWCNTs in the epoxy matrix of a tensile fracture surfaces. Enhancement in tensile strength by 35% and toughness by 53% for a MWCNT loading of 0.75 wt.% in epoxy nanocomposite is the clear indication that, the dispersion of MWCNTs helped in improving anti-corrosion and mechanical properties of MWCNT/epoxy nanocomposite. [50].

**Goyat et al. (2018)** studied the application of Ultrasonic assisted techniques for preparation of TiO<sub>2</sub> nanoparticles reinforcement with epoxy matrix. The study showed that, the level of dispersion of TiO<sub>2</sub> particles into epoxy matrix and different wt. % of loading contents of TiO<sub>2</sub> particles significantly increased the storage modulus, tensile strength and Tg. Also, this signifies that the good interfacial interaction of particles with polymer matrix improved the mechanical properties [51].

**Kumar et al. (2018)** analysed the cluster free homogenous dispersion of MWCNTs (decorating MWCNT surface through  $TiO_2$  nanoparticles) and synthesis of nanocomposites through ultrasonication mixing process followed by axial flow impellor. The effect of low wt.% of  $TiO_2$  nanoparticles on mechanical properties of epoxy composites was investigated. The polymer nanocomposite showed excellent mechanical and anti-corrosion properties. This enhancement in properties was due to the decoration of MWCNTs by  $TiO_2$  nanoparticles [52].

**Maiti et al. (2019)** investigated the EMI shielding response of PVC/MWCNT nanocomposite prepared by solution blending with insulating PVC beads in presence. The region with PVC bead acts as an excluded volume and hence it enhances effective MWCNT concentration to lower the percolation threshold, which thereby enhances electrical conductivity and EMI shielding effectiveness [53].

## 2.3 Gaps identified

Based on the extensive literature survey, following research gaps are identified:

- A lot of study has been carried out to develop polymer nanocomposites by various techniques like extrusion, solution mixing etc. but still it is a challenge to develop cluster free and homogeneously distributed polymer nanocomposites.
- A very limited work has been carried out to develop the cluster free and homogeneously distributed polymer nanocomposite **by ultrasonication dual mixing (UDM) process.**
- Optimization of **ultrasonication dual mixing process** as a function of power, amplitude, time, followed by axial flow impellor parameters for homogeneous distribution of practically cluster free Carbon nanotubes in semi viscous polymer matrix and characterization of properties of polymer nanocomposite, may be a significant step toward current research.
- A very limited work has been carried out to analytically model EMI shielding effectiveness and effective electrical conductivity of nanofibers reinforced polymer composites, considering the tunneling resistance, orientation of CNTs, aspect ratio and other critical factors.

## 2.4 Problem formulation and objective of present study

Based on the introduction and literature review, the primary objectives of present work are as follows:

- Processing of MWCNT/epoxy nanocomposite specimens.
- To study ultrasonication dual mixing process parameters for homogenous dispersion and cluster free epoxy-based nanocomposites and preparation of better characteristics of polymer-based nanocomposites.
- Characterization of improved mechanical properties of MWCNT/epoxy nanocomposites.

- Analytical modelling to find effective electrical conductivity of nanocomposites considering various critical factors.
- Analytical modelling for near field and far field EMI shielding

After completing literature survey, the different parameters used of ultrasonication mixing process are as follows:

- Amplitude (%)
- Time (min)
- Pulse on time (sec)
- Impeller speed (rpm)
- Solvent (wt. %)

# Chapter 3 Experimentation

#### **3.1 Introduction**

This chapter describes the preparation process of MWCNT/epoxy nanocomposite and its characterization for mechanical and viscoelastic properties.

#### 3.2 Materials used

In the present investigation, epoxy resin by the trade name Camcoat 2071 is used as the matrix material with HY951 hardener supplied by Champion Advanced Materials Pvt. Ltd, India. Epoxy resin used here is a medium viscosity bisphenol-A based material employed in coating and fabrication process while HY951 hardener is used owing to the good mechanical and structural properties offered. Powder form of MWCNT used as filler material have an average diameter of 25 nm and length  $10 \,\mu$ m.

#### **3.3 Preparation of polymer nanocomposites**

MWCNT nanoparticles by 0.25 wt.% and 60 mL of acetone are added in the epoxy resin and stirred gently by using a glass rod to obtain a homogeneous adhesive slurry. Ultrasonic processor having a Titanium alloy tip Ti-6Al-4V of 13 mm diameter and power output of 750 W is introduced in the adhesive slurry at an amplitude of 75% to create an ultrasonic wave at a constant frequency of 20 kHz. High intensity ultrasonic waves that propagate through the ultrasonic processor are passed through the adhesive slurry. These waves form vacuum bubbles in the slurry owing to the high- and low-pressure cycles. High pressure cycles break the vacuum bubbles and create extreme shock waves resulting in deagglomeration of MWCNT clusters and thereby increasing the dispersion of particles in the adhesive slurry.



**Figure 3.1** A Schematic diagram of the process for preparation of MWCNT/epoxy nanocomposite by simultaneous application of ultrasonic waves and shear force from Axial flow impeller [52].

Ultrasonic processor is used for a period of 30 minutes operated intermittently for 10 seconds and kept idle for 10 seconds. Further, external cooling is provided around the vessel by adding ice cubes to retain the slurry temperature. The mixture is kept in a hot air oven at 70 °C for 24 hours to evaporate the acetone.



Figure 3.2 Silicon rubber mold

10 wt.% of hardener is mixed into the adhesive mixture evenly through axial flow impellor and vacuum degassing is done to remove the air bubbles from the

composite as depicted in Figure 3.1. Specimens are prepared by pouring the bubble-free MWCNT/epoxy adhesive into the silicon rubber mold. Specimens are cured for 12 hours at 50°C.

Similar procedure is followed to prepare the specimens of epoxy resin reinforced with varying wt.% of MWCNT nanofillers (0.5 and 1 wt%). Table 1 presents the chemical composition and process parameters used in the fabrication of nano-composite.



Figure 3.3 showing (a) Ultrasonicator coupled with magnetic stirrer, (b) Hot air oven,(c) Tensile test and DMA samples, (d) sample for lap shear test of MWCNT/epoxy adhesive joint of aluminium substrate.

After reviewing a lot of research study, the optimum value of ultrasonication mixing process parameter used for preparation of MWCNT/epoxy nanocomposites are listed in Table 3.1, and the other compositions of varying wt. % of MWCNT/epoxy nanocomposites processed using aforesaid process, are as listed in the Table 3.2.

Power Output	750 Watt
Amplitude	60 %
Frequency	20 kHz
Pulse Rate ON/OFF	5 Sec ON And 5 Sec OFF
Impellor Speed (in rpm)	350 rpm

 
 Table 3.1 Optimum value of ultrasonication mixing process parameter used for preparation of MWCNT/epoxy nanocomposites.

Epoxy Resins	<b>MWCNTs Contents</b>	Aliphatic hardener
40 gm	0.0 wt. %	10 wt. %
40 gm	0.25 wt. %	10 wt. %
40 gm	0.5 wt. %	10 wt. %
40 gm	1 wt. %	10 wt. %

 Table 3.2 Different compositions of varying wt. % of MWCNT/epoxy nanocomposites.

#### **3.4 Preparation of faying surface of aluminum substrates**

In order to attain the maximum lap shear strength, the surface of aluminum substrate was prepared by mechanical treatment. In this process, the surface of aluminum substrate was abraded with emery papers of grade 220 to remove the oxide surface from aluminum substrate. The abrasion process of aluminum substrate was done for half an hour to reduce the void formation by removing the dirt and other contaminants from its surface and enhanced the bond strength. The faying surface of aluminum was cleaned by acetone before utilizing the surface [54].

#### **3.5 Mechanical characterization techniques**

#### 3.5.1 Tensile Test

The dumbbell-shaped tensile test specimen (ASTM D-638(V) standard) of pure epoxy and different MWCNT filler loaded nanocomposites were subjected to tensile testing using a Universal Testing Machine (UTM), at a crosshead speed of 1 mm/min at ambient conditions as shown in Fig. 3.4. The tensile strength, elastic modulus, strain to break % and toughness was calculated by stress-strain curves of tensile test specimens. The toughness was obtained from the area under the stress-strain curve and the elastic modulus was estimated from linear fitting of initial portion of the stress-strain curve till strain of 0.3%.



Figure 3.4 Universal testing machine (UTM) used for tensile test

The dimensions of tensile specimen as par the ASTM standard are shown in Fig. 3.5. At least three replicate specimens were tested and their mean values with standard deviation are reported for each composition.



Figure 3.5 Tensile test specimens (a) and dimensions (b) as per ASTM standard

### 3.5.2 Dynamic Mechanical Analysis (DMA)

The Dynamic Mechanical Analysis (DMA) test was used for measuring the visco-elastic behaviour of specimens by DMA testing machine as shown in Fig. 3.6.



Figure 3.6 DMA testing machine (Perkin-Elmer DMA 8000) used for DMA analysis

The cast specimens of neat epoxy and its nanocomposite were initially prepared to accurate dimension of  $9.2 \times 7.5 \times 2.5 \text{ mm}^3$  by fine emery paper polishing according to the requirement of single cantilever bending mode dynamic testing (Fig. 3.7).



Figure 3.7 Single cantilever bending mode of dynamic testing and DMA specimens.

For Dynamic mechanical analysis, Perkin-Elmer DMA 8000 was used on single cantilever bending mode at a fixed frequency of 1 Hz within a temperature range from 30 to 210 °C at a heating rate of 10°C/min according to the standard American Society for Testing and Materials (ASTM) D4065. The experimental parameters used in dynamic mechanical analysis are mentioned in below Table 3.3.

Parameter	Range	Unit
Specimen dimensions	9.5×7.5×2.5	mm <sup>3</sup>
Temperature range	35-210	°C
Heating rate	1	°C/min
frequency	1.0	Hz

**Table 3.3** Experimental parameter of dynamic mechanical analysis

#### 3.5.3 Adhesive joints preparation and Lap Shear Strength Test

Single lap shear joint of aluminum substrate was prepared by applying MWCNT/epoxy nanocomposite as adhesive on different faying surface of aluminum substrate. The adhesive mixture was fluently placed on faying surface

in an appropriate position to form a lap joint by assuring the dimension as shown in Fig. 3.8.

During curing stage, a uniform pressure of 5 MPa was applied on mating surface of aluminum substrate by the roller at a speed of 2 mm/min to obtain a lap joint of an overlapped area of  $12.7 \times 25.4 \text{ mm}^2$  and uniform bond line thickness.



Figure 3.8 Schematic diagram of single lap shear adhesive joint on aluminium substrates [55].

Now the obtained adhesive joint specimens were placed inside a convection oven at a temperature of 50 °C for 6h for curing process. Bond line thickness of adhesive joint was measured by removing the fillets at all the edges and by polishing the specimens. Optical microscope was used for measuring the bond line thickness.



Figure 3.9 Lap Shear Strength test sample before lap shear strength test.

The lap shear test was conducted by placing each end of specimen in the grips of universal testing machine and pulled apart at a speed of 1mm/min. the maximum lap shear strength of adhesive joint was calculated by dividing the maximum load to the lap area. Lap shear strength test sample image before lap shear strength test is shown in Fig. 3.10. The relationship between stress and strain of adhesive joint was recorded by plotting stress and strain curve during lap shear test.

# Chapter 4 Results and discussion

## **4.1 Introduction**

In this chapter, the response of different wt.% of MWCNT/epoxy nanocomposites to tensile test, lap shear strength test and DMA tests have been given and discussed.

#### 4.2 Characterization of MWCNT reinforced epoxy nanocomposites

#### 4.2.1 Tensile Test:

The mechanical properties of the nanocomposites can be easily evaluated by stress-strain curve. The effect of addition of MWCNT nanofiller on tensile strength of nanocomposites was recognized by stress-strain curve as shown in Fig. 4.1. The stress-strain curve was generated according to ASTM D-638 standard. The area under curve represents the toughness of the specimens (Fig. 4.2).



Figure 4.1 Stress-Strain of neat epoxy and MWCNT/epoxy nanocomposites.

Both figures (4.1 and 4.2) indicate that, the nanocomposite with 0.5 wt.% of MWCNT has the highest increase in tensile strength and toughness when compared to pure epoxy composite i.e 19 % and 43.5 % respectively. This was due to preparation of the nanocomposites by nanofiller prepared by Ultrasonic dual mixing process which resulted in cluster free homogeneous dispersion of

MWCNTs in the epoxy matrix. Hence, well bonded contact between nanofibers and matrix is formed which enhances the tensile strength and toughness [56]. The enhancement in tensile strength with increase in weight percentage of MWCNT nanofiller (0.25 wt. % and 0.50 wt. %) in epoxy matrix was 10% and 22.26 % respectively and toughness was 17.24% and 42.54% respectively as compared to neat epoxy. The area under stress-strain curve (toughness) was evaluated by using origin software analysis.

The reinforcement of 1.0 wt.% of MWCNT nanofiller in epoxy matrix considerably reduces the tensile strength (Fig. 4.1) and toughness (Fig. 4.2) of the nanocomposites. Therefore, it is clear that both the mechanical properties, gradually increase with the addition of MWCNT nanofiller up to a level and then decreases. This may be due to the reason that, the increment in nanofiller content leads to the formation of MWCNT clusters which helps degrade the contact between nanofibers and matrix and hence reduce the reinforcing efficiency of the nanofillers. When load is applied, due to weak bonding crack nucleation takes place in the nanocomposites. Hence, it is evident that, the tensile strength and toughness of nanocomposites are primarily influenced by amount of nanofiller, homogenous cluster free dispersion and adhesion interaction of nanofiller with the epoxy matrix [57-58].



Figure 4.2 Toughness properties of neat epoxy and different wt.% MWCNT epoxy nanocomposites.

MWCNT content (wt.%)	Tensile Strength (MPa)	Elastic Modulus (GPa)	Area Under Stress-Strain Curve (MPa)
0.0	58	5.76±0.02	38.38±0.01
0.25	64.184	6.62±0.01	45±0.01
0.5	70.912	6.96±0.03	54.71±0.02
1.0	61.272	7.49±0.01	41.77±0.03

 Table 4.1 Tensile strength and elastic modulus of neat epoxy and different wt.%

 MWCNT/epoxy nanocomposites

#### 4.2.2 Lap Shear Strength Analysis

The effect of MWCNT nanofiller adhesive and neat epoxy adhesive on the lap shear strength of adhesive joint can be characterized by shear stressshear strain curve as shown in Fig. 4.4. Single lap shear adhesive joint was formed by applying neat epoxy adhesive and different wt.% of MWCNT-epoxy adhesive on mechanically treated surface of aluminum metal substrate. A constant rolling load of 5.0 N was applied to produce optimum bond line thickness of adhesive.



Figure 4.3 Lap Shear Strength of neat epoxy and different wt.% MWCNT/epoxy nanocomposites.

The faying surface of aluminum metal substrate was mechanically prepared to enlarge bonding area and good mechanical interlocking to achieve higher bond strength. The average result of three specimen of equal weight percentage was taken for better analyzing the result of lap shear test. Fig. 4.3 shows that the lap shear strength of nanocomposite adhesive joint has slightly increased with increase in MWCNT nanofiller content from neat epoxy to 0.5 wt.% followed by further decrease in strength with increase in nanofiller content to 1.0 wt.%. The loading of 0.5 wt.% of MWCNT/epoxy adhesive joints shows maximum enhancement in lap shear strength upto 21% as compared to neat epoxy adhesive joints. This is due to the cluster free homogenous dispersion of MWCNT nanofiller in epoxy matrix that attributes to transfer maximum stress from epoxy matrix to the MWCNTs and high specific surface area of MWCNTs improved the degree of crosslinking with strong interfacial interaction between the MWCNT nanofiller and epoxy matrix [59].

MWCNT contents (wt.%)	Lap Shear Stress (MPa)	Strain (%)
0.0	6.8	554.54
0.25	7.23	588.46
0.5	8.23	645.44
1.0	6.99	576.33

 Table 4.2 Lap Shear Stress vs Strain (%) data of different wt.% MWCNT/epoxy nanocomposites.

The variation in weight percentage of MWCNT/epoxy adhesive joint i.e. 0.25, and 0.5 wt.% give enhancement of 6.27%, and 21% respectively in lap shear strength as compared to neat epoxy adhesive joint. The figure shows that, the ductility (strain %) also increases with increase in the MWCNT nanofiller content in epoxy adhesive joint up to 0.5 wt.%, after this it gradually decrease with increase in the weight percentage of nanofiller. The high loading of

MWCNT nanofiller leads to MWCNT cluster formation, which decrease the lap shear strength of nanocomposite adhesive joints.

#### 4.2.3 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis was carried out to measure viscoelastic behaviour and load bearing capacity of the nanocomposite material. It is a simple method to obtain storage modulus (G'), loss modulus (G") and tan delta (Tan  $\delta$ ) of polymer nanocomposites by measuring its stiffness and damping. The load bearing capacity of MWCNT/epoxy nanocomposites increases from low modulus epoxy matrix to the high modulus MWCNT/epoxy nanocomposite.



**Figure 4.4** Storage Modulus (MPa) vs Temperature (°C) of neat epoxy and different wt.% of MWCNT/epoxy nanocomposites.

Fig. 4.4 indicates, how the variation in weight percentage of MWCNT nanofiller affects the storage modulus of epoxy resins. In glassy region, the value of storage modulus with respect to the temperature of neat epoxy is low. It is clear that, the increment in weight percentage of MWCNT nanofiller in epoxy matrix enhances the storage modulus due to the cluster free homogenous dispersion and good adhesion interfacial interaction. Some studies also suggest that the increase in the storage modulus is due to high covalent bonding between MWCNTs and epoxy matrix [60]. The reinforcement of 0.5 wt.% of MWCNT nanofiller in epoxy matrix shows highest storage modulus i.e. 1269 MPa. This

may be due to cluster free homogenous distribution that leads to the higher degree of cross-linking between the MWCNT nanofiller with 3D network of epoxy matrix which results in decreasing the molecular chain mobility and enhancing the storage modulus [61]. The enhancement in storage modulus with increase in weight percentage of MWCNT nanofiller (i.e. 0.25 wt.% to 0.5 wt%) in epoxy matrix is 5.65% and 17.5% respectively as compared to neat epoxy.

The storage modulus of 1.0 wt.% of MWCNT nanofiller has been slightly decreased due to the formation of clusters in epoxy matrix. The formation of clusters in epoxy matrix increases the molecular chain mobility which reduces storage modulus. It was observed that, the value of storage modulus of neat epoxy as well as different loadings of nanofiller in epoxy matrix decreases with increase in temperature, when the temperature reaches to glass transition temperature ( $T_g$ ). This steady decrease in storage modulus near glass transition temperature credits the molecular chain mobility. Glass transition temperature is the temperature in which, transformation of thermosetting polymer occurs from glassy or rigid state to rubbery state.



Figure 4.5 Tan  $\delta$  vs. Temperature (°C) of neat epoxy of neat epoxy and different wt.% of MWCNT/epoxy nanocomposites.

Loss factor (tan  $\delta$ ) is the ratio of loss modulus to storage modulus, G"/G'. It is a dimensionless number. The larger area under tan  $\delta$  peak

recommends higher energy dissipation. The addition of MWCNT nanofiller to the epoxy matrix leads to the decrease in the area under the tan  $\delta$  peak. This shows interaction of nanofiller increase the interfacial bonding and hence molecular chain mobility at interface decrease, which results in decreasing the damping peak [62]. The glass transition temperature (T<sub>g</sub>) and loss factor (tan  $\delta$ ) of neat epoxy is 68.85 °C and 1.175 respectively (Fig. 4.5). The addition of MWCNT nanofiller (i.e. 0.25 wt.% to 0.5 wt%) in epoxy matrix, slightly increases the glass transition temperature (T<sub>g</sub>) from 77.15 °C to 83.78 °C and decrease the value of tan  $\delta$  from 0.711 to 0.486 respectively. This happened due to the cluster free homogenous dispersion and good interfacial interaction of MWCNT nanofiller into epoxy matrix. The value of tan  $\delta$  of 1 wt.% of MWCNT nanofiller in epoxy matrix is 1.0978 that indicates high non-elastic strain property of nanocomposites.

MWCNT nanofiller contents (wt.%)	Glass transition temperature (Tg)	Storage modulus at glassy region (at 35°C)	Storage modulus at rubbery region (at Tg+35°C)	Loss factor (tan δ)
0.0	68.85 °C	1080 MPa	10.08 MPa	1.1753
0.25	77.15 °C	1141 MPa	16.8 MPa	0.711
0.5	83.78 °C	1269 MPa	20.16 MPa	0.4864
1.0	67.86 °C	989 MPa	23.38 MPa	1.0978

**Table 4.3** Glass transition temperature (Tg), storage modulus (MPa), & loss factor  $(\tan \delta)$  of different weight percentage of MWCNT/epoxy nanocomposites

The damping in MWCNT/epoxy nanocomposite occurs due to the interfacial slippage between epoxy matrix and MWCNTs. When MWCNTs are homogenously distributed then interfacial slippage is very less. As MWCNT nanofiller content increases, clusters are formed which increase the interfacial slippage. The factors affecting the damping characteristics of MWCNT/epoxy nanocomposites is filler percentage, critical shear stress, structural

characteristics and crosslinking of nanofiller with epoxy. The high aspect ratio and high specific surface area of carbon nanotubes also improved damping properties of polymer nanocomposites [63]. The homogeneous dispersion and good interfacial interaction of MWCNT nanoparticles in epoxy matrix is the key aspect of high storage modulus and low loss factor.

# Chapter 5 Micromechanical analysis of effective elastic properties of GRPC

#### **5.1 Introduction**

Polymer nanocomposites act as an outstanding structural material that have very low density and exceptional mechanical, thermal and optical properties. Therefore, these materials are widely used in various application such as in automobile, coating and paints industries, medical equipment, consumer goods and aerospace industry [64-68]. The exceptional properties of polymer nanocomposite primarily depend upon the nanofiller reinforced with polymer matrix. Several nanofillers are available such as nanofibers, nanoclays and nanoparticles, that can easily mix with polymer matrix in achieving desired properties.

Graphene is an excellent two-dimensional nanofiller since its discovery by Geim and Novoselov in 2004 [69-71]. The high mechanical strength and specific surface area (SSA) of graphene make it an appealing for application in polymer composite material. In fact, single layer of graphene with tensile strength of 130 GPa and Young's modulus of 1000 GPa, is the strongest material discovered till date [72]. However, the homogenous dispersion and good interfacial interaction of graphene in polymer matrix is the key issue addressed in fabrication of polymer nanocomposite [73]. Several research studies have been done previously based on mechanical, thermal and electrical properties of graphene reinforced multifunctional polymer nanocomposite. For example, Kalaitzidou et al. [74] dispersed exfoliated graphite nanoplatelets into polypropylene matrix by using melt mixing and injection molding technique. The results reveal that a low loading content of graphene enhanced the elastic modulus, flexural and impact strength of graphene reinforced polymer composite material. Stankovich et al. [75] have reported graphene based polystyrene composites exhibited a percolation threshold of  $\sim 0.1$  volume percent for room-temperature electrical conductivity. Wang et al. [76] used insitu emulsion polymerization technique for synthesis of graphene nanosheetspolystyrene nanocomposites and studied their electrical conductivity and

thermal stability. Tripathi et al. [77] used different technique for preparation of graphene oxide-PMMA nanocomposites. Results reveal that the conductivity depend upon the amount of graphene oxide and method of preparation of polymer composite.

In past decades, the effective mechanical properties of composite materials were predicted by developing various micro-mechanical model. For instance, Thostenson et al. [78] studied the elastic modulus by using Halpin–Tsai theory in terms of the constituent properties, microstructural and geometric parameters. Song and Youn [79] predict the effective elastic properties of composite by using asymptotic expansion homogenization method. Ying ji et al. [80] studied the micromechanical analysis of graphene reinforced polymer composite by using micromechanical M T method. Giannopoulos and Kallivokas [81] predict the effective elastic properties of graphene-based composite by using multi scale FE approach. Selmi et al. [82] studied several micromechanical models for the prediction of effective elastic properties of single walled carbon nanotube reinforced composite. Kundalwal and Ray [83] developed the mechanics of materials approach (MOM) to estimate the effective elastic properties of fuzzy fiber reinforced composite.

In this study, the mechanics of materials (MOM) approach has been derived to predict the effective elastic properties of GRPC. Two-phase model has been developed by considering graphene as a fiber and PMMA as a matrix. To estimate the interphase effect on elastic properties, the additional interphase ZrO<sub>2</sub> nanoparticles has been introduced and three-phase MOM approach has been performed. Further, we use FE simulation to estimate the mechanical properties of two- and three-phase GRPC.

#### **5.2 Modelling**

#### **5.2.1 Effective Elastic Properties of GRPC**

The MOM approach was primarily created by Kundalwal and Ray [84] in 2011 to predict the effective elastic properties of isotropic materials. Certain assumption has been made to construct RVE of GRPC: (i) graphene is uniformly dispersed in PMMA matrix, (ii) there is perfect bonding between graphene and PMMA matrix, (iii) they follow iso-field condition. The representation of RVE of GRPC is shown in figure 5.1, where graphene acts as a solid fiber and PMMA act as a matrix. The resulting composite is free from voids and graphene fiber is homogenously distributed in PMMA matrix.

#### 5.2.2 Two-phase MOM approach

The stress and strain relationship of individual phases of proposed GRPC can be written as

$$\{\sigma^r\}_{6\times 1} = [\mathcal{C}^r]_{6\times 6} \{\varepsilon^r\}_{6\times 1} \tag{1}$$

where, r = g, p, and nc

where  $\sigma^{r}$  denotes the stresses,  $\epsilon^{r}$  strains, and C<sup>r</sup> denotes elastic constant of a matrix. The superscript r used for g, p, and nc which represent graphene fiber, PMMA matrix and GRPC nanocomposite respectively.



Figure 5.1 Representation of cross section of RVE of two-phase GRPC.

Here, we assume perfect bonding between the graphene fiber and PMMA matrix. Therefore, by using rule of mixture and iso-field condition, the equation can be written as:

$$\left\{\varepsilon_3^g\right\} = \left\{\varepsilon_3^p\right\} = \left\{\varepsilon_3^{nc}\right\} \tag{2}$$

$$v_{g}\{\sigma_{3}^{g}\} + v_{p}\{\sigma_{3}^{p}\} = \{\sigma_{3}^{nc}\}$$
(3)

In equation (3),  $v_g$  and  $v_p$  represents the volume fraction of graphene and PMMA matrix respectively. By correlating the equations (1)-(3). stress and strain can be written as follows:

$$\{\varepsilon^{nc}\}_{6\times 1} = [V_1]_{6\times 6}\{\varepsilon^g\}_{6\times 1} + [V_2]_{6\times 6}\{\varepsilon^p\}_{6\times 1}$$
(4)

$$\{\sigma^{nc}\} = [\mathcal{C}_1]\{\epsilon^g\} + [\mathcal{C}_2]\{\epsilon^p\}$$
(5)

From equation 2, we can write as

$$[\mathsf{C}_3]\{\varepsilon^{\mathsf{g}}\} - [\mathsf{C}_4]\{\varepsilon^{\mathsf{p}}\} = 0 \tag{6}$$

$$[V_3] = [V_1] + [V_2] [C_4]^{-1} [C_3]$$
(7)

$$[V_4] = [V_2] + [V_1] [C_3]^{-1} [C_4]$$
(8)

$$[\mathcal{C}^{nc}] = [\mathcal{C}_1] [\mathcal{V}_3]^{-1} + [\mathcal{C}_2] [\mathcal{V}_4]^{-1}$$
(9)

Here, matrix from  $[C_1]-[C_4]$  and  $[V_1]-[V_4]$  are obtained by using some assumptions and curtailments. The matrix  $[C^{nc}]$  in Eq. 9 gives the effective elastic properties of the obtained GRPC.

#### 5.2.3 Three-phase MOM approach

Three-phase MOM model was created to recognize the interphase effect on effective elastic properties of GRPC. Each constituent must be fully utilized to obtain optimum mechanical performance of GRPC. It is only possible when there is a certain interaction between graphene fiber and PMMA matrix.



Figure 5.2 Representation of cross section of RVE of three-phase GRPC.

In current study,  $ZrO_2$  nanoparticles are introduced as an interphase to improve the mechanical properties of GRPC. The addition of  $ZrO_2$  interphase significantly improved the bonding interaction between graphene and PMMA matrix. Thus, the load bearing capacity of GRPC increases. From figure 5.2, based on the principal material coordinate axes (1–2–3), the constitutive relations for the constituent phases of three-phase GRPC are written as

$$\{\sigma^r\}_{6\times 1} = [\mathcal{C}^r]_{6\times 6} \{\varepsilon^r\}_{6\times 1} \tag{10}$$

where, r = g, p, i and nc

In Equation (10), g, p, i and nc denote graphene fiber, PMMA matrix,  $ZrO_2$  interphase and GRPC nanocomposite respectively. To satisfy the perfect bonding condition between graphene and the neighboring phases, iso-stress and iso-strain conditions, and rule of mixture can be expressed as,

$$\left\{\varepsilon_3^g\right\} = \left\{\varepsilon_3^p\right\} = \left\{\varepsilon_3^i\right\} = \left\{\varepsilon_3^{nc}\right\}$$
(11)

$$\{\sigma_{33}\} = v_g\{\sigma_{33}^g\} + v_i\{\sigma_{33}^i\} + v_p\{\sigma_{33}^p\}$$
(12)

In Eq. (12),  $v_p$ ,  $v_g$  and  $v_i$  represent the volume fraction of PMMA matrix, graphene fiber and ZrO<sub>2</sub> interphase respectively, present in the RVE. Substituting eqn.. (10) into eqn.. (11) and (12), the corresponding stress and strain vectors of GRPC can be written as:

$$\{\sigma\} = [C_1]\{\varepsilon^g\} + [C_2]\{\varepsilon^i\} + [C_3]\{\varepsilon^p\}$$
(13)

$$\{\varepsilon\} = [\mathsf{V}_1]\{\varepsilon^g\} + [\mathsf{V}_2]\{\varepsilon^i\} + [\mathsf{V}_3]\{\varepsilon^p\}$$
(14)

$$[C_4]\{\varepsilon^g\} - [C_5]\{\varepsilon^i\} = 0 \tag{15}$$

$$[C_5]\{\varepsilon^i\} - [C_6]\{\varepsilon^p\} = 0$$
(16)

Finally, the effective elastic coefficient of GRPC can be obtained as

$$[C] = [C_1] [V_5]^{-1} + [C_7] [V_6]^{-1}$$
(17)  
where,

 $[C_7] = [C_3] + [C_2] [C_5]^{-1} [C_6],$   $[V_4] = [V_3] + [V_2] [C_5]^{-1} [C_6],$   $[V_5] = [V_1] + [V_4] [C_6]^{-1} [C_4],$  $[V_6] = [V_4] + [V_1] [C_4]^{-1} [C_6]$ 

Here, matrix from  $[C_1]-[C_6]$  and  $[V_1]-[V_6]$  are obtained using some assumptions and curtailments.

#### 5.2.4 Tensile Test

The predicted elastic properties obtained from two- and three-phase MOM modelling technique are introduced to perform tensile test simulation using ANSYS 18.2. The dimensions of the tensile test specimen have been shown in figure 5.3, which follow ASTM D 638 standard.



Figure 5.3 Dimension of tensile Test Specimen

Figure 5.4 Dimension of tensile Test Specimen

The tensile test specimen with required dimension is firstly created by using a 3D Computer Aided Drawing (CAD) modelling software. The mechanical properties of GRPC with fiber volume fraction,  $V_f = 0.1$  are introduced in ANSYS 18.2 software. The previously created tensile test specimen by CAD software, is then imported into ANSYS workbench by using 'import geometry option'. The specimen is meshed to fine shells and boundary conditions are applied (see figure 5.4), that means the face marked as 'A' is fixed with no displacement in any direction and the load is applied on the red face marked as 'B' in positive x-direction. The obtained deformation curve varies with change in applied load. Similarly, the same procedure is followed with varying volume fraction from 0.1 to 0.5. Further, the load vs extension curve is plotted for different volume fraction of GRPC.

#### **5.3 Results and Discussion**

The predicted value of effective elastic properties of two- and threephase GRPC are evaluated by using mechanics of material (MOM) approach. The effect of  $ZrO_2$  interphase on mechanical properties are demonstrated. Further, the effective elastic properties are used for tensile test simulation and predicted tensile results are expressed in load vs extension curve for different volume fraction.

#### 5.3.1 Effective elastic properties and effect of ZrO2 interphase

The mechanical properties such as elastic modulus 'E' and Poisson's ratio 'v' of graphene fiber,  $ZrO_2$  nanoparticles and PMMA matrix are summarized in Table 5.1.

	Elastic modulus	Poisson's ratio	References
	(01 4)	Tutto	
Graphene	985	0.26	Kundalwal et al.
			2018 [85]
ZrO <sub>2</sub>	200	0.28	Cousland et al., 2018
interphase			[86]
PMMA	2.963	0.38	Ayatollahi and
matrix			Torabi, 2010 [87]

Table 5.1 Elastic properties of the constituent phases of GRPC

These mechanical properties are used for prediction of effective elastic properties of GRNC. The variation in effective elastic coefficient  $C_{11}^{GRPC}$  of GRPC with varying graphene fiber volume fraction (V<sub>f</sub>) are shown in figure 5.5 (a). It is observed that the addition of ZrO<sub>2</sub> interphase enhanced the interfacial bonding between the PMMA matrix and graphene fiber. Thus, the magnitude of  $C_{11}^{GRPC}$  increases with respect to fiber volume fraction.





**Figure 5.5** Variation of (a)  $C_{11}^{GRPC}$  and (b)  $C_{12}^{GRPC}$  of the GRPC with varying graphene fiber volume fraction.

Similar results have also been obtained for the value of  $C_{12}^{GRPC}$  as plotted in figure 5.5 (b). Results show that, the values of  $C_{12}^{GRPC}$  for two- and three-phase increases with increase in graphene volume fraction. The addition of ZrO<sub>2</sub> interphase slightly increases the curve of  $C_{12}^{GRPC}$  for three-phase GRPC. Similar response is also predicted for effective elastic coefficients  $C_{23}^{GRPC}$  of transversely isotropic GRPC as shown in figure 5.6 (a).



**Figure 5.6** Variation of (a)  $C_{23}^{GRPC}$  and (b)  $C_{33}^{GRPC}$  of the GRPC with varying graphene fiber volume fraction

Two straight-line curves are obtained from two- and three-phase MOM model respectively as shown in figure 5.6 (b). This is because, the radially grown graphene is being aligned along the  $3^{rd}$  direction enhances the axial stiffness of the GRPC along the  $3^{rd}$  direction which indicates iso-strain condition of GRPC. Therefore, the elastic properties of GRPC increases. It is noteworthy that the area between the two straight line increases with increase in fiber volume fraction, that means the addition of ZrO<sub>2</sub> interphase enhanced the bonding interaction between fiber and matrix.

The EEC  $C_{44}^{GRPC}$  of the nanocomposite also shows the same trend with respect to graphene volume fraction V<sub>f</sub> as shown in figure 5.7. ZrO<sub>2</sub> interphase enhanced the effective elastic properties of GRPC. It should be noted that both two- and three-phase MOM approaches evaluate the EEP by assuming perfect bonding condition between PMMA matrix and graphene fiber, with and without considering the interphase.



Figure 5.7 Variation of  $C_{44}^{GRPC}$  of the GRPC with varying graphene fiber volume fraction.

#### **5.3.2** Tensile test results

The obtained tensile test results for two-phase GRPC are shown in figure 5.8 (a). The load vs extension curve plot for two-phase indicates the deflection of varying volume fraction of graphene fiber in GRPC. At same loading (2000 N) condition, the deflection curve decreases from 1.73 mm to 0.98 mm with increase in volume fraction of graphene fiber from 0.1 to 0.5 respectively.



Figure 5.8 Load vs extension curve for a GRPC (a) for varying graphene fiber volume fraction, (b) two and three-phase NC

As we know that the stiffness of a material is inversely proportional to extension. Therefore, the strength and stiffness of GRPC increases with increase in graphene fiber volume fraction. This is due to the perfect bonding interaction between the graphene fiber and PMMA matrix. Similarly, the tensile test is now simulated for three-phase GRPC. The load vs extension curve for three-phase GRPC is shown in figure 5.8 (b). When we introduce  $ZrO_2$  interphase in two-phase GRPC and applied the same load (2000 N), the extension curve decreases. That means the strength and stiffness of three-phase GRPC increases.

This shows that, the addition of interphase enhanced the bonding quality between the fiber and matrix, therefore the strength and stiffness of GRPC nanocomposite increases.

# Chapter 6 An analytical methodology to evaluate the EMI S.E of epoxy/CNT Nanocomposites in C-band by the role of tunneling conductivity of CNTs

#### **6.1 Introduction**

Whenever any electronic devices performed their intended function, they radiate some electric and magnetic energy. These induced radiation produces different kind of pollution in the field of electronics application especially in wireless and communication system [88-92]. The excessiveness of these radiation in environment causes electromagnetic interference (EMI), which alter the performance of other electronic devices and also, hazardous for living environment [93-96]. Therefore, it is assumed that electromagnetic interference is the curse for electronic devices. Hence, in order to prevent the electronic devices from electromagnetic interference, some shielding materials (known as EMI shielding materials) are placed, that block and reduce the effect of interfering electric as well as magnetic energy. The efficiency of EMI shielding material is measured in terms of shielding effectiveness (SE) which is a powerful function of interfering EM source's and the enclosure's characteristics. Frequency, amplitude, wave impedance and polarization are the tools of the interfering EM source's characteristic, while material permeability, thickness, permittivity, conductivity, etc. are the tools of the enclosure's characteristics. Among all of these, electrical conductivity and type of interfering EM source are in dominating nature [97-99].

Different type of polymers such as polyester, epoxy, vinyl ester, polypropylene etc. are used as a shielding material in EMI shielding applications. [100-103]. Among them, epoxy resin is the most widely used structural polymer having exceptional properties such as high mechanical and adhesive properties, low shrinkage, good chemical resistance, and ease of

processing [104-106]. However, it has very poor electrical conductivity that offer constraint to achieve desired shielding effectiveness when devices work at high frequency range [107-110]. To overcome this issue, we introduced a conductive nanofiller such as carbon nanotubes in epoxy matrix that not only enhanced their electrical conductivity but also improved mechanical and thermal properties [111-122]. For instance, He et al. [107] studied the electrical and thermal properties of MWCNT/epoxy nanocomposite experimentally by changing the weight percentage of CNTs and found that the electrical and thermal properties of nanocomposite depend upon weight percentages and distribution of CNTs in epoxy matrix. Cardoso et al. [108] reported that electrical conductivity of CNT/epoxy nanocomposites increased with increase in loading content of CNT nanofiller. However, the percolation threshold of CNT/epoxy nanocomposite was reported lower than 0.1 wt. % of CNTs. Lee et al. [109] fabricated MWCNT/epoxy nanocomposites using fluorinated MWCNT by surface treatment of MWCNT in fluorine gas. The EMI shielding effectiveness of the fluorinated nanocomposites enhanced up to 26% with increasing fluorination extent. Kumar et al. [123] studied the EMI shielding effectiveness of graphene/TiO<sub>2</sub> hybrid epoxy nanocomposites and reported that the total shielding effectiveness of graphene/TiO<sub>2</sub> hybrid epoxy nanocomposites is -11 dB compared to neat epoxy having value -3 dB. Serna et al. [124] examined the shielding effectiveness of nanocomposite experimentally with the help of electronic mode stir chamber and band limited white Gaussian noise and validated the obtained experimental results with the predicted analytical value. They found that the shielding effectiveness obtained from experimental results is less than the predicted analytical value.

From the above studies, it can be concluded that the incorporation of CNTs in epoxy matrix enhanced the mechanical, electrical and EMI shielding properties of nanocomposites. The high aspect ratio and high specific surface area of CNTs improve the density of conductive network in a polymer matrix which increases the charge transfer. Consequently, the electrical conductivity of nanocomposite improved, which resulted in improving its shielding effectiveness. Various models have been developed previously to simulate the electrical properties of nanocomposites [125-129]. However, their design must

overcome important barriers involved with the control phenomena between their interfaces and fabrication methods to achieve desired results [130, 131]. It has been found that the CNTs makes a three dimensional (3-D) complex network with epoxy matrix above a critical concentration, that indicates the percolation threshold [132-134]. The percolation threshold is that point at which electrical conductivity increases sharply with increase in concentration of CNTs. The percolation threshold is a very powerful full function of the aspect ratio of CNTs because it is achieved when a smooth connection took placed between the CNTs. Higher the length of CNTs (results a higher aspect ratio) leads a better connection between the CNTs [135, 136]. The electrical conductivity of CNTpolymer nanocomposite depends upon various factor such as nanotubes types (single-walled carbon nanotubes and multi-walled carbon nanotubes) [137], nanotubes waviness [138], nanotubes length [139], contact resistance between nanotubes [140]. All these parameters come in the domain of the tunneling effect. The tunneling effect is a mechanism for determining the electrical conductivity of CNT-polymer nanocomposites by transferring the electrons between nanotubes [141]. However sometimes, the CNT are not perfectly connected to their surrounding CNTs, so neighboring CNT transfer charges by electron jumping. From previous studies, it has been found that several research articles have reported the EMI shielding effectiveness of CNT-epoxy nanocomposites, but till now, there is no research articles available that investigates the tunneling effect on EMI shielding effectiveness of CNT-epoxy nanocomposites. Therefore, it is of great interest to investigate the tunneling effect CNTs on the EMI shielding behavior of CNT-epoxy nanocomposites.

In this work, the electrical conductivity of CNT-epoxy nanocomposites is evaluated analytically by considering the effect of change in CNT waviness, CNT interphase thickness and CNT aspect ratio with simultaneous change in weight percentage of CNTs. In addition, the role of interphase thickness, aspect ratio and waviness on the percolation threshold of CNTs are also studied. The EMI shielding effectiveness of CNT-epoxy nanocomposites is estimated analytically by considering tunneling effect of CNT in epoxy matrix in C- band (4-8.2 GHz) region. The shielding effectiveness is calculated by changing the weight percentage of CNT as well as sample thickness of CNT-epoxy nanocomposites.

# Nomenclature $\sigma_{N}$ Electrical conductivity of CNT $\sigma_{\rm m}$ Electrical conductivity of matrix $\sigma_{ND}$ Conductivity of tunneling distance of CNT Conductivity of waviness CNT $\sigma_{_{Nw}}$ Relative conductivity of nanocomposite $\sigma_r$ Distance between nano particles S Contact area of CNT а Resistance of tunneling distance between CNT Rs R<sub>N</sub> Resistance of CNT R<sub>ND</sub> Effective electrical resistance R Radius of CNT 1 Length of CNT Equivalent length of waviness CNT leq f Percentage of networked CNT Percolation threshold volume fraction φ<sub>p</sub> $\phi_{\text{eff}}$ Effective volume fraction of effective CNT Vex Excluded volume of CNT V Volume of CNT Interphase thickness t Waviness factor u b Thickness of shielding materials δ Skin depth
- d Screen distance
- f Frequency of electromagnetic waves
- μ Magnetic permeability
- $\mu_0 = 4\pi \times 10^{-7} \text{ H/m}$
- $\mu_r$  Relative permeability

#### 6.2 Analytical modeling

In this section, different model is derived to study the electrical conductivity and EMI shielding of CNT-epoxy nanocomposites by treating CNT as a solid cylinder of circular cross-sectional area, not hollow tubes. Also, it is notable that CNT is randomly distributed inside epoxy matrix for making the conductive network [125].

#### 6.2.1 Simulation of electrical conductivity

The theoretical model of electrical conductivity of CNT-polymer nanocomposites was proposed by Ryvkina et al. [142] by considering the tunneling distance between the CNTs and is expressed as:

$$\sigma_{\rm s} = Y \exp(-Xs) \tag{1}$$

where, s, X and Y denotes the distance between nanoparticles, characteristic tunnel distance and constant parameter respectively. From the above eqn., if the value of "s" is high means the distance between nanoparticles is more, than it simulates very low conductivity. Whereas, if the distance between the nanoparticles is zero (i.e. s = 0) then "Y" parameter can be considered as a conductivity of CNT ( $\sigma_N$ ) and eqn. (1) can be modified as:

$$\sigma_{\rm s} = \sigma_{\rm N} \tag{2}$$

Also, the value of "X" was suggested as 2 which presents accurate results compared to experimental data. Finally, eqn. (1) can be written as:

$$\sigma_{\rm s} = \sigma_{\rm N} \exp(-2s) \tag{3}$$

Feng et al. [126] evaluated the electrical resistance of the distance between CNT as:

$$R_{s} = \frac{s}{a\sigma_{s}}$$
(4)

where "a" and "R<sub>s</sub>" represent contact area of CNT and resistance of tunneling distance between CNTs respectively.

Takede et al. [127] studied the tunneling distance between the CNT, they assumed extended nanotubes and inter-nanotubes region of CNT as a filler network. They proposed two types of conductive networks between CNT dominated by different nanotubes contact configuration as shown in Fig. 1. One conductive network is developed due to overlapping of CNT as shown in Fig. 1 (a). For this conductive network, they suggested that the contact area at an overlapping position is  $4R^2$ . While the other conductive network is developed due to the in-plane contact configuration as shown in Fig. 1 (b). For this conductive network, the contact area is equal to the cross-sectional area of nanotubes i.e.  $\Pi R^2$ . Finally, an average contact area was taken by considering both configurations. The value of this contact area is approximated  $3R^2$ , which gives:

$$R_{s} = \frac{s}{3R^{2}\sigma_{s}}$$
(5)

where "R" is the radius of CNT





Now, put the value of  $\sigma_s$  from eqn. (3) into the eqn. (5), the resistance of tunneling distance between CNT is given as:

$$R_{s} = \frac{s}{3R^{2}\sigma_{N} \exp\left(-2s\right)}$$
(6)

The total electrical resistance of CNT is the summation of resistance induced due to the CNT and resistance induced due to the tunneling distance, term as effective electrical resistance ( $R_{ND}$ ) and gives as:

$$\mathbf{R}_{\rm ND} = \mathbf{R}_{\rm N} + \mathbf{R}_{\rm s} \tag{7}$$

where " $R_N$ " is the resistance of CNT given as:

$$R_{\rm N} = \frac{1}{\Pi R^2 \sigma_{\rm N}} \tag{8}$$

where "l" is the length of the CNT. Applying eqn. (6) & (8) into eqn. (7) the effective resistance of CNT is demonstrated as:

$$R_{\rm ND} = \frac{s}{3R^2\sigma_{\rm N}\exp\left(-2s\right)} + \frac{1}{\Pi\,R^2\sigma_{\rm N}} \tag{9}$$

Now, the conductivity of tunneling distance of CNT can be written from the eqn. (8) as:

$$\sigma_{\rm ND} = \frac{l_{\rm ex}}{\Pi \, (R_{\rm ex})^2 \, R_{\rm ND}} \tag{10}$$

where " $l_{ex}$ " and " $R_{ex}$ " is the length and radius of extended CNT, respectively. Here " $l_{ex}$ " is considered as the length of CNT because the length of CNT is more than the tunneling distance. Also, the extended radius is equal to CNT radius because tunneling distance does not offer any impact on the radius of CNT. Eqn. (10) can be expressed as:

$$\sigma_{\rm ND} = \frac{1}{\Pi R^2 R_{\rm ND}} \tag{11}$$

Put the value of  $R_{ND}$  from eqn. (9) into eqn. (11), the electrical conductivity of extended CNT is estimated as:

$$\sigma_{\rm ND} = \frac{l}{\prod R^2 \left[ \frac{s}{3R^2 \sigma_{\rm N} \exp\left(-2s\right)} + \frac{l}{\prod R^2 \sigma_{\rm N}} \right]}$$
(12)

Here, the value of  $\Pi$  is near about 3.14. So, after solving the above eqn..

We can express as:

$$\sigma_{\rm ND} = \frac{1 \,\sigma_{\rm N}}{\frac{s}{\exp(-2s)} + 1} \tag{13}$$

The above eqn. represents the electrical conductivity of CNT by considering tunneling distance. Now, this calculated electrical conductivity of CNT can be used to develop the model to evaluate electrical conductivity of CNT/epoxy nanocomposites by considering tunneling mechanism.

Dang and Zheng [125] developed a model to evaluate the electrical conductivity of CNT-polymer nanocomposites beyond the percolation threshold by assuming the straight CNT randomly distributed inside polymer matrix and is given as:

$$\sigma = \sigma_{\rm m} + \frac{f \phi_{\rm f} \sigma_{\rm N}}{3} \tag{14}$$

where " $\sigma_m$ , f and  $\phi_f$ " represents the electrical conductivity of polymer matrix, percentage of networked CNT and CNT volume fraction respectively. If the polymer matrix is an insulator by nature then their electrical conductivity is very less as compared to the CNT. So, neglect the value of " $\sigma_m$ ".

Now, substituting the value of from eqn. (13) into above eqn. the conductivity of CNT-polymer nanocomposites with tunneling effect is demonstrated as:

$$\sigma = \frac{f \, l \, \phi_f \sigma_N}{\frac{3s}{\exp(-2s)} + 3l} \tag{15}$$

The above model represents the electrical conductivity of CNT-polymer nanocomposites in terms of CNT network by considering tunneling effect. However, this model does not regard the influence of interphase and CNT curvature on electrical conductivity, while these terms significantly affect the percolation threshold and the percentage of networked fillers.

Berhan et al. [143] proposed a model based on the percolation threshold for CNT in CNT-polymer nanocomposites. They assumed that CNT nanofiller were randomly dispersed in nanocomposites and expressed as:

$$\phi_{\rm p} = \frac{V}{V_{\rm ex}} \tag{16}$$

where " $V_{ex}$ " and "V" represents the excluded volume and volume of CNT, respectively. Excluded volume is defined as that volume in which the center of the same particle can't arrive.

Also, they suggest the expression of "V" and " $V_{ex}$ " for random distribution of CNT in CNT-polymer nanocomposites as:

$$V = \Pi R^2 1 + \frac{4 \Pi R^3}{3}$$
(17)

$$V_{ex} = \frac{32}{3} \prod R^3 \left[ l + \frac{3}{4} \left( \frac{l}{R} \right) + \frac{3}{32} \left( \frac{l}{R} \right)^2 \right]$$
(18)

Baxter et al. [129] considered the interphase layer thickness at a percolation threshold. They found that interphase zone decreases the excluded volume. However, the interphase layer surrounding CNT leads to the development of the conductive network. Then excluded volume given as:

$$V_{ex} = \frac{32}{3} \Pi (R+t)^3 \left[ l + \frac{3}{4} \left( \frac{l}{R+t} \right) + \frac{3}{32} \left( \frac{l}{R+t} \right)^2 \right]$$
(19)

where "t" is the interphase thickness.

In addition, the high aspect ratio of CNTs have the tendency to form waviness and reduced the effectiveness of conductivity. Fig 2 (a & b) represents the straight and waviness of CNT. Let " $l_{eq}$ " is the equivalent length of waviness CNT concerning the straight CNT and "u" is the waviness factor defined as:

$$u = \frac{l}{l_{eq}}$$
(20)

From eqn. (20), it is concluded that higher the value of "u" given more waviness and less effective length. However, w = u shows the CNT without waviness.

Now, by putting the value of effective length of CNT from eqn. (20) into eqn. (19). The excluded volume assuming interphase and CNT waviness is described as:

$$V_{ex} = \frac{32}{3} \Pi \left( R + t \right)^3 \left[ l + \frac{3}{4} \left( \frac{l/u}{R+t} \right) + \frac{3}{32} \left( \frac{l/u}{R+t} \right)^2 \right]$$
(21)

Now, assumed eqn. (17) and eqn. (21) into eqn. (16). The percolation threshold of CNT can be expressed as:

$$\phi_{p} = \frac{\Pi R^{2} l + \left(\frac{4}{3}\right) \Pi R^{3}}{\frac{32}{3} \Pi (R+t)^{3} \left[ l + \frac{3}{4} \left(\frac{l/u}{R+t}\right) + \frac{3}{32} \left(\frac{l/u}{R+t}\right)^{2} \right]}$$
(22)

The above eqn. represents the percolation threshold of CNT with incorporation of interphase and waviness of CNT.



Figure 6.2 (a) Straight CNT (b) waviness CNT [57].

Feng et al. [126] suggested a model for CNT and their surrounding interphase and termed as effective CNT as shown in Fig. 6.3. They found that effective CNT changes the general properties of CNT-polymer nanocomposites. Also, they proposed effective volume fraction of effective CNT considering the important of CNT interphase and waviness and express as:



Figure 6.3 Effective CNT with interphase [57].

However, only a number of CNT are employed in the continuous networked after percolation, while others are dispersed in CNT-polymer nanocomposites. Then the percentages of a network of percolated CNT is expressed as:

$$f = \frac{(\phi_{eff})^{1/3} - (\phi_p)^{1/3}}{1 - (\phi_p)^{1/3}}$$
(24)

Deng and Zheng [125] found that the waviness of CNTs deteriorates the conductivity of CNTs and expressed as:

$$\sigma_{\rm Nw} = \frac{\sigma_{\rm N}}{u} \tag{25}$$

The proposed eqn. for " $\phi_{eff}$ ", "f" and " $\sigma_N$ " terms can be assumed in eqn. (15) to predict the electrical conductivity of CNT-polymer nanocomposites based on tunneling mechanism by the roles of CNT interphase, waviness of CNT, tunneling distance and aspect ratio of CNT.

#### 6.2.2 Simulation of EMI shielding

Sevgi [99] proposed a theoretical model in 2009 for EMI shielding effectiveness. He put a conductive shielding plate of infinite extent in between EM rays emitted device and EM rays absorbed by device for calculating the shielding effectiveness.



Figure 6.4 An EM shielding material with demonstrate of absorption, reflection and multiple reflection losses.

It is noted that, shielding of a material is cumulative effect of absorption, reflection and multiple internal reflections. However, absorption is a major

shielding mechanism and reflection is a secondary shielding mechanism as shown in Fig. 6.4. Further, the multiple internal reflections are neglected, when shielding effectiveness due to absorption is more or equal to 10 dB.

Shielding effectiveness (in dB) due to absorption is given as:

$$SE_{A} = 20 \log_{10} \left[ \exp \left( \frac{b}{\delta} \right) \right]$$
(26)

where "b" and " $\delta$ " represents the thickness of shielding materials and skin depth respectively. The tendency of penetration of the EM waves in a conductor material is known as skin depth and it is measured in meter. Therefore, skin depth is expressed as:

$$\delta = \sqrt{\frac{2}{\omega \, \sigma \, \mu}} \tag{27}$$

where " $\omega$ " is angular frequency ( $\omega = 2\Pi f$  and "f" is the frequency of EM waves in Hz) of incident EM wave and " $\mu$ " is the magnetic permeability ( $\mu = \mu_0\mu_r$ , where  $\mu_0 = 4\pi \times 10^{-7}$  H/m and  $\mu_r$  is the relative permeability). Now eqn. (27) is modified as:

$$\delta = \frac{0.066}{\sqrt{f \,\sigma_{\rm r} \,\mu_{\rm r}}} \tag{28}$$

Now, assume eqn. (28) into eqn. (26), the shielding effectiveness due to absorption loss is expressed as:

$$SE_A = 131.4 b \sqrt{f \sigma_r \mu_r}$$
(29)

where " $\sigma_r$ " is the relative conductivity of CNT-polymer nanocomposites with respect to copper in S/m. (Given as:  $\sigma_r = \sigma/\sigma_{cu}$ ,  $\sigma_{cu} = 5.87 \times 10^7$ S/m) [99].

The shielding effectiveness from reflection can be demonstrated in terms of the wave impedance ( $Z_w$ ) and the conductor impedance ( $Z_s$ ) as:

$$SE_{R} = 20 \log_{10} \left(\frac{E_{i}}{E_{t}}\right) = 20 \log_{10} \left[\frac{(Z_{s} + Z_{w})^{2}}{4 Z_{s} Z_{w}}\right]$$
(30)

where " $E_i$ " and " $E_t$ " represents the strength of incident electric field and transmitted electric field respectively.

Furthermore, the impedance of shielding material is given as (in  $\Omega$ ):

$$Z_{s} = \sqrt{\frac{\omega\mu}{\sigma}}$$
(31)

Also, for the far field, the (plane) wave impedance in free space is expressed as (in  $\Omega$ ):

$$Z_{w} = Z_{o} = 120 \ \Pi \tag{32}$$

Therefore, assuming eqn. (31) and (32) in eqn. (30), we get:

$$SE_{R} = 20 \log_{10} \left[ \frac{1}{4} \sqrt{\frac{\sigma_{r}}{\mu_{r} f}} \right] = 168 + 10 \log_{10} \left[ \frac{\sigma_{r}}{\mu_{r} f} \right]$$
(33)

However, in the near field, the type of interfering source is a key factor. The wave impedance for magnetic source is  $Z_{wm} = Z_o (2\Pi d/\lambda) \Omega$ . Where  $\lambda = 3x \ 10^8/f$ . Therefore, the shielding effectiveness of reflection (SE<sub>R</sub>) for magnetic source can be express as:

$$SE_{Rm} = 14.6 + 10 \log_{10} \left[ \frac{f \ d^2 \sigma_r}{\mu_r} \right]$$
(34)

where "d" is the screen distance.

While, wave impedance for electrical source is  $Z_{we} = Z_o (\lambda / 2 \Pi d) \Omega$ .

Therefore, the shielding effectiveness of reflection  $(SE_R)$  for magnetic source can be expressed as:

$$SE_{Re} = 332 + 10 \log 10 \left[ \frac{\sigma_{r}}{\mu_{r} f^{3} d^{2}} \right]$$
 (35)

The SE due to reflection is calculated on the basis of following condition.

If  $d \le \frac{\lambda}{2\Pi}$  then, either eqn. (34) or eqn. (35) is used depends upon the source of generation of EM waves. However, eqn. (33) is used for all other cases.

Therefore, the total SE is expressed as:

$$SE_{T} = SE_{A} + SE_{R} \tag{36}$$

After specifying the input parameters and the type of interfering source, we can calculate the shielding effectiveness caused by the absorption using eqn. (29), and also checks whether the interfering source is in the near or far-field region. We can calculate the shielding effectiveness caused by the reflections according to either eqn. (33) or eqn. (34) and (35). Finally, the total shielding effectiveness is summation of contribution from absorption, and reflection as given in eqn. (36).

#### 6.3 Results and discussion

In this section, the tunneling effect of CNTs on the electrical conductivity and EMI shielding properties of CNT-epoxy nanocomposites with the help of developed model are given and discussed. The primary factors such as aspect ratio, waviness and interphase thickness are evaluated separately with respect to the weight percentage of CNTs. The EMI shielding effectiveness of CNT-epoxy nanocomposites are evaluated analytically in C- band (i.e. 4-8.2 GHz) with respect to the weight percentages of CNTs as well as thickness of CNT-epoxy nanocomposites.

#### **6.3.1 Effect of aspect ratio on electrical conductivity**

As already mentioned, the aspect ratio of CNT is one of the important factors affecting the percolation threshold of nanocomposites. The typical electrical conductivity curves with respect to weight percentage of CNTs at different aspect ratio are shown in Fig. 6.5. In this analysis, we assumed that the conductivity of CNT is  $10^4$  S/cm and other physical parameters of CNT are taken as R = 15 nm, u = 1.54, t = 1 nm and s = 8.5 nm. The aspect ratio of CNT-epoxy nanocomposites varies by changing the length of CNTs from 5 µm to 8 µm with an increment of 1 µm.

From Fig. 6.5, it has been found that electrical conductivity of CNTepoxy nanocomposites is increased with increase in the wt. % of CNTs as well as length of CNTs. It is well known that the epoxy act as an insulator with conductivity range of  $10^{-14}$  S/m. Therefore, the electrical conductivity of CNTepoxy nanocomposites is nearly 0 at  $\phi_f < 1$  wt. %. Furthermore, the electrical conductivity of CNT-epoxy nanocomposites ramped up with increase in the wt. % of CNTs as well as their aspect ratio. Also, a remarkable change in electrical conductivity is obtained with increasing the weight percentage of CNT (1 wt. % to 5 wt. %) in CNT-epoxy nanocomposites.



Figure 6.5 Electrical conductivity of nanocomposite at different wt. % of nanofillers and different aspect ratio.

A denser network of CNT is developed with increasing in the weight percentage of CNTs and thus, this sharp increase in electrical conductivity indicates the existence of percolation threshold. The maximum electrical conductivity is observed around 15 S/m at  $\phi_f = 5$  wt. % and  $l = 8 \mu m$ . Therefore, the increase in weight percentage and length of CNT gives a positive effect on the electrical conductivity of CNT-epoxy nanocomposites. It is clear that, the random distribution of small weight percentage of CNTs in epoxy matrix can form a percolated conductive chain which helps in increasing the electrical conductivity of CNT-epoxy nanocomposites. However, the higher loading of CNTs above the percolation threshold enhances the density of the CNT network which increases the charge transfer. Previous study reported the similar effect of " $\phi_f$ " parameter on tunneling conductivity of CNT-epoxy nanocomposites [127, 145]. In addition, the results also revealed that the larger the length of CNTs, higher will be the electrical conductivity. This is because, larger CNTs can produce a bigger and denser network inside the epoxy matrix that allows better moment of the electron [135, 136]. Arenhart et al. [146] also reported the positive role of CNTs length on tunneling conductivity of CNT- polymer nanocomposites.

#### 6.3.2 Effect of interphase thickness on electrical conductivity

The variation of electrical conductivity at different interphase thickness "t" and different wt. % of CNT are shown in Fig. 6. Here the physical parameters of CNT are assumed as R = 15 nm, u = 1.54, l = 8  $\mu$ m and s = 8.5 nm and the interphase thickness vary from 0.5 nm to 2 nm with an increment of 0.5 nm. It has been found that electrical conductivity of CNT-epoxy nanocomposites increases with increase in the interphase thickness. Results showed that the electrical conductivity of CNT-epoxy nanocomposites is close to 0 for all values of "t" when  $\phi_f < 1$  wt. %. The highest electrical conductivity is obtained at  $\phi_f = 5$  wt. % and t = 2 nm, which is 23 S/m. This proved that the very thick interphase and high CNT concentration provide high tunneling conductivity.



Figure 6.6 Electrical conductivity of nanocomposite at different wt. % of nanofillers and different interphase thickness.

The interphase thickness generates a layer around CNTs which produces a conductive network at low CNT concentration. On the other hand, an effective CNT (Fig. 6.3) is developed in nanocomposites by combining the CNT tubes and interphase which enhanced the " $\phi_{eff}$ ". Many nanotubes employ for networking in interphase which efficiently leads the level of percolated CNT in the network. Therefore, it has been assumed that interphase thickness also plays a positive role in the percolation threshold, effective CNT and the percentage of networked CNT. Accordingly, a high level of interphase thickness undoubtedly improves the electrical conductivity of CNT-epoxy nanocomposites. Previously

study also demonstrated the similar effect of interphase thickness on the percolation threshold and tunneling conductivity of CNT- polymer nanocomposites [126]. Therefore, the role of "t" parameter in tunneling conductivity of CNT-epoxy nanocomposites is well justified in the presented model.

#### 6.3.3 Effect of waviness on electrical conductivity

Fig. 6.7 shows the electrical conductivity versus weight percentage of CNT curves at different waviness factor of CNT. The physical parameters of CNT are taken as R = 15 nm, t = 1 nm,  $l = 8 \mu m$  and s = 8.5 nm. The waviness of the CNT changes the equivalent length of CNT (Fig. 6.2), undoubtedly it changes the waviness factor as mentioned in eqn. (20). The equivalent length of CNT is varied from 5.6  $\mu m$  to 8  $\mu m$  with an increment of 0.8  $\mu m$  each time, which changes the waviness factor from 1 to 1.43.



Figure 6.7 Electrical conductivity of nanocomposite at different wt. % of nanofillers and different waviness factor.

As shown in Fig 6.7, due to the extremely low electrical conductivity of epoxy, the electrical conductivity of CNT-epoxy nanocomposites is near about 0 at  $\phi_f < 1$  wt. % and for all values of "u". With the addition of CNT, the electrical conductivity enhances sharply and maximum electrical conductivity is obtained as 27 S/m at u = 1 and  $\phi_f = 5$  wt. % of CNT, which reveal that the increase in the waviness of CNT bottom out the electrical conductivity of CNT-epoxy nanocomposites.

So, the effective length of CNT is determined by "u" parameter. A low value of CNT waviness factor shows a poor waviness which demonstrates a poor curvature of CNT in CNT-epoxy nanocomposites and increases the effectiveness of tunneling conductivity. This is because, the increase in waviness of CNT reduced the effective length of CNT which reduced the conductive network between them. Therefore, the electrons cannot jump quickly as they get blocked in epoxy matrix which results in poor electrical conductivity. On the other hand, the waviness of CNT reduces the effect of CNT on the network levels that results in formation of insulated network. Previous study also demonstrated the similar effect of the CNT waviness on electrical conductivity of CNT-polymer nanocomposites [147, 148]. Therefore, the present model effectively justified the role of "u" on the tunneling conductivity of CNT-epoxy nanocomposites.

#### 6.3.4 Effect of CNT concentration on EMI shielding

As mentioned in modelling section, the total shielding effectiveness evaluated from eqn. (36) is the summation of contribution from absorption, and reflection. Furthermore, shielding effectiveness is calculated by considering tunneling conductivity of CNT-epoxy nanocomposites by assuming another parameter such as as R = 15 nm, u = 1.1,  $l = 8 \mu m s = 8.5$  nm, t = 1 nm, d = 30cm and b = 5 mm. Fig. 6.8 depicts the frequency dependency of EMI shielding responses of CNT-epoxy nanocomposites in C-band (4-8.2 GHz) at different wt. % of CNT.

Increase in the concentration of CNT offers a positive effect on shielding effectiveness due to absorption as shown in Fig. 6.8 (a) while it offers a negative role on shielding effectiveness due to reflection as shown in Fig. 6.8 (b). Because, by increasing the concentration of CNT, a more conductive network in a matrix is generated, so that it can absorb all the electromagnetic radiation which falls on it rather than reflect it. The total shielding effectiveness of CNT-epoxy nanocomposites with 1 wt. % CNTs is approximately the same as 2 dB, in the considered frequency range as shown in Fig. 6.8 (c).



Figure 6.8 EMI shielding at different wt. % of CNT (a) due to absorption, (b) due to reflection and (c) total EMI shielding of ECNT nanocomposites.

However, total shielding effectiveness is increasing with increasing the concentration of CNT. A higher wt. % CNT offers a dense conductive network, that can effectively transfer the electron. Consequently, the electrical conductivity of CNT-epoxy nanocomposites is increasing which significantly increases the total shielding effectiveness. The total shielding effectiveness of nanocomposites at 5 wt. % of CNT is varied from 35 dB to 45 dB, indicating that it can be used for commercial applications. Moreover, it is seen that shielding effectiveness increases sharply from 1 wt. % to 2 wt. % of CNT and after that, it increases moderately. Because after 2 wt. % CNT, further addition of CNT is not uniformly dispersing due to agglomeration of CNT in matrix. Another reason is that, percolation threshold occurred in between 1 wt. % to 2 wt. % of CNT which causes remarkable change in the electrical conductivity in this range.

The EMI shielding effectiveness of the nanocomposites is almost independent of frequency for the lower filler content, but total shielding effectiveness experiences remarkable hike in value for a higher CNT content in a CNT-epoxy nanocomposite. On the other hand, adding of CNT in nanocomposites reflect a positive effect on EMI shielding of CNT-epoxy nanocomposites. The same pattern of CNT concentration addition on the EMI shielding effectiveness was reported in different papers [90-93]. So, the developed model properly justifies the previous studied in terms of CNT concentration.

#### 6.3.5 Effect of thickness on EMI shielding

In this, the thickness of CNT-epoxy nanocomposites varies to find out their influence on EMI shielding effectiveness in the domain of tunneling conductivity. Tunneling conductivity is calculated with the help of developed model assumed as R = 15 nm, u = 1.1,  $l = 8 \mu m s = 8.5$  nm d = 30 cm and t = 1nm at 4 wt. % of CNT. The thickness of CNT-epoxy nanocomposites varies from 1 mm to 5 mm with an increment of 1 mm each time.



Figure 6.9 EMI shielding at different thickness of nanocomposites (a) due to absorption, (b) due to reflection and (c) total EMI shielding of ECNT nanocomposites.

As the thickness increases, shielding effectiveness due to absorption is also increase as shown in Fig. 6.9 (a). However, increase the thickness of CNTepoxy nanocomposites causes no influence on shielding effectiveness due to reflection as shown in Fig. 6.9 (b). As mentioned in the simulation part, shielding effectiveness due to reflection is not a function of the thickness of nanocomposites that's why it does not play any role to change the shielding effectiveness due to reflection. Fig. 6.9 (c) demonstrates the pattern between total shielding effectiveness and thickness of CNT-epoxy nanocomposites in a C- band region.

As shown, shielding effectiveness is near about 11 dB obtained at 1 mm thickness of CNT-epoxy nanocomposites and a negligible change is found from 4 to 8.2 GHz. However, increasing the thickness of CNT-epoxy nanocomposites shows increase in the shielding effectiveness. The total shielding effectiveness of CNT-epoxy nanocomposites increases from 30 dB to 38 dB at 5 mm thickness of nanocomposites from 4 to 8.2 GHz. So, the combined effect of both factors gives an increase in shielding effectiveness. In other words, shielding effectiveness due to absorption dominates the total shielding effectiveness at high sample thickness. So, it can say that increase the thickness of the sample ramp up the total shielding effectiveness of CNT-epoxy nanocomposites. The effect of sample thickness on EMI shielding effectiveness was indicated the same phenomenon in previous literature [112, 113].

# Chapter 7 Conclusions and Future scope

### 7.1 Conclusions

In this chapter, the outcome and key understanding of the present work are concluded as follows.

- Ultrasonication mixing process has been efficiently used to disperse MWCNT nanofiller homogenously within the epoxy matrix at loading upto 0.5 wt.%.
- 2. At relatively higher loading of MWCNT nanofiller (1.0 wt.%), the MWCNT-epoxy nanocomposites do not appreciably improve performance due to the formation of clusters.
- At optimum level of CNTs content, MWCNT (0.5wt.%) nanofiller in epoxy nanocomposite, enhancement in tensile strength (19%), lap shear strength (21%), toughness (43.5%), glass transition temperature (23.53%), and storage modulus (17.5%) when compared to pure epoxy composite was evident.
- 4. The significant enhancement in MWCNT-epoxy properties as compared to neat epoxy is primarily attributed to the better capability of the ultrasonication mixing technique to resolve the clusters of CNTs in the epoxy matrix.
- 5. The predicted effective elastic properties of GRPC from the mechanics of materials approach, increased with increment in volume fraction of graphene. Also, the addition of ZrO<sub>2</sub> interphase between the fiber and PMMA matrix significantly enhanced the effective elastic properties of three-phase GRPC.
- 6. the load vs deflection curve obtained by performing tensile test, shows that the strength and stiffness of GRPC increases with increase in volume

fraction of fiber. Also, the addition of interphase significantly enhanced the strength and stiffness of GRPC.

- 7. The random distribution of small weight percentage of CNTs in epoxy matrix can form a percolated conductive chain which helps in increasing the electrical conductivity of CNT-epoxy nanocomposites. However, the higher loading of CNTs above the percolation threshold enhances the density of the CNT network which increases the charge transfer.
- The CNT concentration, length, interphase thickness and tunneling conductivity cause positive effects on the electrical conductivity of CNTpolymer nanocomposites. However, least waviness and tunneling resistance is preferred for the conductivity.
- 9. The total shielding effectiveness increases with increment in the concentration of CNT, because SE is directly proportional to electrical conductivity. Hence, when the CNT concentration increases, so does the conductivity, which thereby helps SE to increase. At higher wt. % CNT offers a dense conductive network that can effectively transfer the electron.
- 10. By increasing the CNT content, shielding due to reflection  $(SE_R)$  decreases but the shielding due to absorption  $(SE_A)$  increases. Also, the extent of increase in SE<sub>A</sub> is very high compared to extent of decrease in SE<sub>R</sub>. Hence, the overall SE increases.
- 11. By increasing the specimen thickness, the overall conductivity increases. However, only  $SE_A$  increases with increase in material thickness, whereas,  $SE_R$  remains constant, as it is independent of the specimen thickness.  $SE_A$  solely contributes to the overall SE as  $SE_R$  remains constant, hence the overall SE increases with increase in material thickness.
- 12. Overall, for use of MWCNT/epoxy nanocomposites in EMI shielding sectors, the optimum MWCNT concentration should be selected such

that, the all the properties are enhanced without the agglomeration of MWCNTs.

#### 7.2 Future Scope

1. Fatigue and creep testing of the epoxy nanocomposites as well as lap shear testing of the epoxy nanocomposites adhesive based joints of different metal substrate such as aluminium and mild steel should be identified. The elevated temperatures for nanocomposites can be done to correlate the cohesive and adhesive properties in order to utilize the knowledge for advanced applications of epoxy nanocomposites mainly in aerospace and automobile industries.

2. The homogeneous dispersion for CNT reinforced epoxy composite has been achieved. But further optimization of process parameters in terms of amplitude, processing time and impeller speed for further breaking of agglomerated CNTs up to individual CNT on higher loading of CNTs can be done.

3. The use of other type of filler such as single walled carbon nanotubes, graphene, carbon fiber, carbon nano-bead and glass fiber, to see the effect on mechanical, electrical and EMI shielding of epoxy composite using ultrasonication dual mixing technique.

4. The detail studies of epoxy nanocomposites interface, which plays a major role to improve the properties of the nanocomposite can be done to correlate the properties in order to utilize the knowledge for advanced applications of nanocomposites mainly in aerospace and automobile industries.

5. Based on the analytical predictions and suggestions, desired EMI shielding of the nanocomposite can be achieved experimentally to verify the results.

6. The analytical model can be verified by numerical models to see the limitations of the analytical model.

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