Manufacturing of nanocomposites filled with carbon nanofibers for electromagnetic waves absorption

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- Electromagnetic fields
- " waves
- Electric waves.

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Final Approval

It is certified that the work presented in this thesis entitled **"Manufacturing of Nanocomposites filled with carbon nanofibers for electromagnetic waves absorption"** by **Abdul Mateen,** registration No.131-FBAS/MSPHY/F12 is of sufficient standard in scope and quality for the award of degree of MS Physics from Department of Physics, International Islamic University, Islamabad, Pakistan

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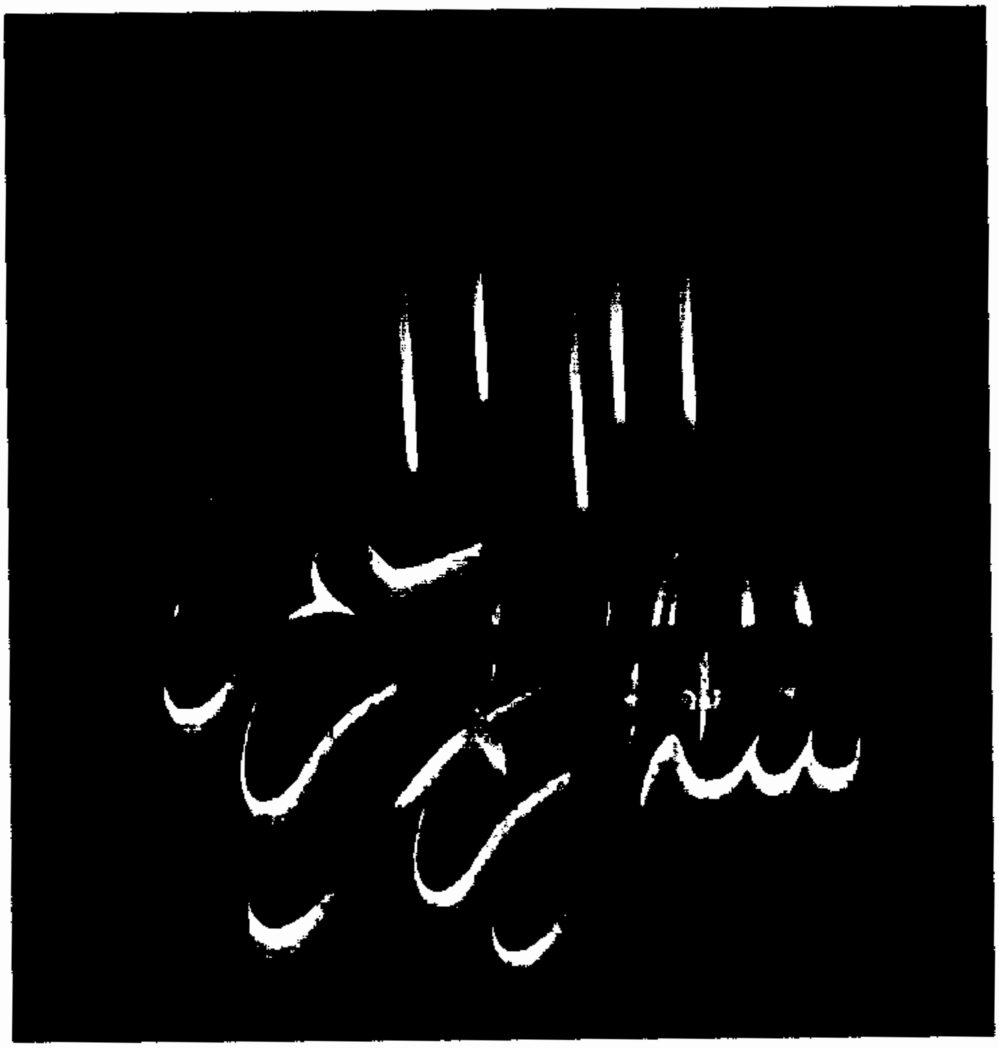

DEDICATED
To
My beloved
Grand father
Mother
Sisters
Brothers
And
CUTE
Siam Sarmad

Declaration

I **Abdul Mateen** (Registration # 131-FBAS/MSPHY/F12), student of MS Physics (session 2012-2014), hereby declare that the matter presented in the thesis titled **"Manufacturing of nanocomposites filled with carbon nanofibers for electromagnetic waves absorption"** is my for own work and has not been published or submitted as research work or thesis in any form in any other university or institute in Pakistan or aboard.

Abdul Mateen
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Dated: ____________________

Forwarding Sheet by Research Supervisor

The thesis entitled "**Manufacturing of nanocomposites filled with carbon nanofibers for electromagnetic waves absorption**" submitted by **Abdul Mateen** (Registration # 131-FBAS/MSPHY/F12) in partial fulfillment of M.S degree in Physics has been completed under my guidance and supervision. I am satisfied with the quality of his research work and allow him to submit this thesis for further process to graduate with Master of Science degree from Department of Physics, as per IIU Islamabad rules and regulations.

Dated: ______________________

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Acknowledgment

All praises and prayers be to **ALMIGHTY ALLAH** who created this universe and **DROOD O SALAM** upon his Last Holy prophet Hazrat MUHAMMAD (peace be upon him), who raised the flag of Islam in this humanity. It is only to thank ALLAH that I have completed this research work.

I am very thankful to my Supervisor of this project Dr. Kashif Nadeem and Co-supervisor Dr. Aqeel Ahsan Khurram , who helped me during research work and gave me very useful information's and provided several related research papers about my project. I can never forget his kindness behavior. At the completion of my project; I can never forget the best guidance granted by my best teachers, Prof. Dr. Kareem Shah.

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Abdul Mateen

Abstract

Nanocomposites filled with carbon nanofibers were prepared and characterized for use in electromagnetic radar absorbing material with minimum thickness. Four different kinds of nanocomposites sheets (CNF-2, CNF-3, CNF-4 and CNF-5) were prepared at different carbon nanofibers weight fraction (2wt%, 3wt%,4wt% and 5wt%) for sandwich structure by solution processing techniques by using acetone. Their reflection loss (RL), transmission loss and complex permittivity were measured in frequency range of 11-18 GHz by free space method. While dc electrical conductivity of these absorbing sheets were measured by four probe method. The minimum reflection loss in carbon nanofiber absorbing sheets was -2.5 dB at 18 GHz frequency. Reflection loss can be manipulate by making hybrid nanocomposites with multiwall carbon nanotubes (MWCNTs) and graphene with (0.5 wt%) in carbon nanofibers absorbing sheets. In multi wall carbon nanotubes hybrid nanocomposites, the minimum reflection loss was -9.48 dB at 18 GHz frequency, while in graphene hybrid nanocomposites the minimum reflection loss was -9.78 dB at 11.2 GHz frequency.

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Chapter :1

Introduction and Literature Review

1.1: Electromagnetic waves

Electromagnetic wave is a specific form of electromagnetic field produced by accelerating charges. Electromagnetic waves consist of electric and magnetic field components propagate perpendicular to one another and also perpendicular to the direction of propagation of waves. These waves can travel with the speed of light in vacuum [1]. On the basis of wavelength electromagnetic waves are sub divided into seven types.

Table 1.1: *Different types of electromagnetic waves* [2].

Name	**Wavelength**	**Frequency**
Gamma rays	less than 0.02 nm	more than 15 EHz
X-rays	0.01 nm-10 nm	30 EHz - 30 PHz
Ultraviolet	10 nm-400 nm	30 PHz - 750 THz
Visible	390 nm-750 nm	770 THz - 400 THz
Infrared	750 nm-1 mm	400 THz-300 GHz
Microwave	1 mm-1 m	300 GHz-300 MHz
Radio	1 mm-10,0000 km	300 GHz-3Hz

1.1.1: Microwaves

Microwave is a particular form of electromagnetic waves having wavelength ranges from 1mm to 1m and frequency ranges from 300 GHz to 300 MHz. It lies in between infrared and radio waves. Microwaves can passes easily through glass and ceramics materials but it is absorbed by water, matter with water contents and carbon materials. Microwaves are used for communication between ground and satellites for various electronic equipments such as radar, mobile phone and television etc. Microwaves can be sub divided into eight bands on the basis of frequency as shown in table 1.2.

Table 1.2: *Sub division of microwaves.*

Bands	Frequency (GHz)	Wavelength (cm)
L	1-2	30-15
S	2-4	15-7.5
C	4-8	7.5-3.8
X	8-12	3.8-2.5
Ku	12-18	2.5-1.7
K	18-26	1.7-1.1
Ka	26-40	1.1-0.75
V	40-75	0.75-0.40

1.2: Electromagnetic interference (EMI)

Electromagnetic interference (EMI) occurs, when unwanted signals of transmitter superimposes with the signals of receiver. These unwanted signals are produced by various electronic devices used in commercial and scientific applications. Electromagnetic interference can degrade the performance of electronic equipments [3]. Nowadays it has become a great problem for rapid development of electronic devices such as mobile phone, loud speaker, television and radio reception etc.

1.2.1: Sources of electromagnetic interference

There are basically two sources of electromagnetic interference.

1.2.1.1: Natural sources of EMI

Naturally occurring electromagnetic sources are related to lightning and sunspots originate from Sun and galaxies, which can disturb the effectiveness of electronic devices. When communication satellite comes in between Sun and Earth, then Sun can affect the performance of satellite, but this occurs in minor cases.

1.2.1.2: Man-made sources of EMI

The common man made sources of electromagnetic interference are laptop, mobile phone, dc motors, television, radio broadcasting stations and over had cables etc. Mostly electromagnetic interference occurs in radio frequency range [4].

1.2.2: Elements of electromagnetic interference

Electromagnetic interference depends on three elements.

1.2.2.1: Emitting devices

Emitting devices are the electronic devices which can emits electromagnetic radiation and disturb the performances of other electronic devices. These electronic equipments depend on the frequency of electromagnetic radiation. Electromagnetic radiation having high frequency can transfer very minimum electromagnetic energy to small electronic equipment and very high frequency electromagnetic radiation can transfer no energy at all. But electromagnetic radiations can affect electronic devices seriously having frequency between 10 kHz to 1 GHz.

Typically in normal operation a cell phone can transmits 600 mW power to the surrounding , but when it is ringing it can transmits 2 W power [5]. Similarly a radio set can transmit 2-5 W power in normal operation to the surrounding. New wireless network and Bluetooth are operating at higher frequency and produces lower electromagnetic radiation as compared to cell phone.

1.2.2.2: Distance between source and receiver

EMI depends on the distance between source and receiver. Electromagnetic energy falls inversely to the square of distance, if the distance between source and receiver increases. All clinical equipments are safe, if their distance from the source is at least 1m [6].

1.2.2.3: Affected devices

Affected devices are the electronic components of electrical devices, which cannot work properly in electromagnetic environments. To eliminate electromagnetic interference problem, modern electronic devices are shielded by using conductive shield to perform work properly in electromagnetic environments. Combination of LC circuits can also be used for shielding, because LC circuits transfer electromagnetic energy into heat energy.

1.2.3: Coupling mechanism of EMI

Electromagnetic magnetic interference occurs by two coupling path.

- Radiated coupling (electric or magnetic field coupling)
- Conductive coupling (current or voltage coupling)

1.3: Electromagnetic shielding

Electromagnetic shielding is a mechanism by restricting the electromagnetic radiation into a space (OR) by blocking them with obstacle made of conducting materials. These conducting materials are specifically applied as enclosure to separate electronic devices from outside electromagnetic environment. So the conducting materials which can protect electronic devices from outside electromagnetic signals are called shielding [7]. Due to recent development of electromagnetic equipments such as mobile phone, radar technology, laptop and television etc emits low level of electromagnetic signals which interfere with others electronic equipments and becomes a big problem for human beings. To reduce effects of electromagnetic interference various protective materials are used as a shield such as metals, carbons fibers and graphite materials etc.

1.3.1: Mechanism of electromagnetic shielding

When electromagnetic wave passes through a certain conducting medium, then it can interact with the mobile charge carriers (electrons or holes) of the conducting medium. The interaction of electromagnetic waves can be classified into three categories. Fig.1.1 shows shielding effect by obstacle. When electromagnetic waves are incident on a certain obstacle, a part of these waves ware reflected, a part ware transmitted and a part of these waves ware absorbed.

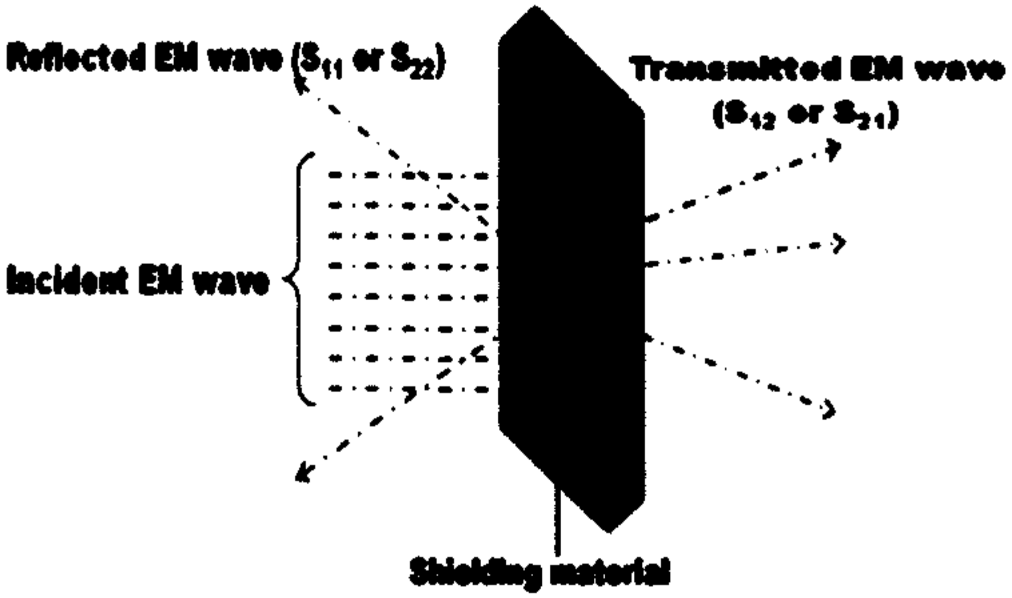

Fig. 1.1: *Shielding mechanism by reflection and absorption of electromagnetic waves [1].*

1.3.1.1: Reflection

The first method of electromagnetic shielding is reflection. To shield a material by reflection mechanism, the shielding material must possess mobile charge carrier which can interact with incoming electromagnetic radiation. Shielding materials must be electrically conducting having approximate volume resistivity 1Ωcm but not necessary high conductivity. Shielding by reflection can be increased by increasing the filler connectivity.

Thus reflection process depends strongly on the obstacle conductivity, permittivity, and frequency but it is independent of thickness of conducting medium. Conducting medium is made from metals coated with electroplating or vacuum deposition [8]. This acts as a Shielding for electromagnetic radiation. Due to high conductivity Silver, Aluminum, Gold and Copper are commonly used for electromagnetic shielding.

1.3.1.2: Absorption

The secondary process of electromagnetic shielding is absorption. For sufficient absorption of electromagnetic radiations, shielding materials should posses magnetic and/or electric dipoles which can interact with incoming electromagnetic radiations. These electric and magnetic dipoles of materials are polarized due to electric and magnetic field of radiation and absorbed electromagnetic radiation. These dipoles are provided by materials having high electric permittivity such as $BaTiO_3$ and magnetic permeability such as Fe_3O_4 [3]. Magnetic permeability may be increased by decreasing domain walls by using multilayer magnetic films. Shielding by absorption mechanism increases with increasing electromagnetic wave frequency. Electromagnetic radiations are absorbed due to moment of mobile charge carriers and polarization of electric and magnetic dipoles of shielding material.

1.3.1.3: Multiple internal reflections

The third process of electromagnetic shielding is multiple internal reflections, which occurs due to reflection of different surfaces in the shielding materials. This process requires a shielding materials having large surface area with small holes line up in a sequence. The holes at one side of shielding are preferred, which will scatter electromagnetic signals in one direction. Internally produced electromagnetic signals can also passes through these holes due to which internally electromagnetic interference may not occur. The incident electromagnetic waves depend on the threshold frequency of small hole and also on surface area of shielding. If the size of opening is 1/20 of the wavelength of interference signals, then it will provide shielding of 20 dB.

The electromagnetic waves at frequency of 1-5 MHz penetrate only near surface region of a conductor known as skin effect. The electric field of electromagnetic waves incident on a conductor decreases exponentionaly with the increase in depth of conductor. The depth of conductor at which the value of electric field becomes 1/e of the incident value as known skin depth, it can be written as,

$$\delta = 1 \Big/ \sqrt{\pi f \mu \sigma} \qquad (1.1)$$

The skin depth decreases with increase in electrical conductivity, permeability and electromagnetic wave frequency. Due this reason skin depth is smaller in nickel as compared to copper.

1.4: Shielding of electronic components

All electronic devices such as mobile phone, radio, loud speaker and laptop work properly only, if they are shielded from outside electromagnetic waves, which can interfere with these devices and degrade their performance. So shield can protect electronic equipments from electromagnetic interference.

1.4.1: Shielding effectiveness

Shielding effectiveness is the logarithmic ratio of incident energy to the transmitted energy. When electromagnetic radiation passes through a shielding material, a part that electromagnetic energy is obserbed, a part is reflected, while remaining energy is transmitted. Electromagnetic wave propagates in the form of electric and magnetic fields perpendicular to one another and also perpendicular to the direction of propagation of wave. Electromagnetic shielding posses two region [9].

- Near field region

If the distance between transmitting source and shield as smaller than ($\lambda/2\pi$), then the shielding region is near field region.

- Far field region

If the distance between transmitting source and shield is larger than ($\lambda/2\pi$), then the shielding region is far field region. Shielding effectiveness is the logarithmic ratio of incident to transmitted electric or magnetic fields and can be expressed as

$$SE = 20 \log \ (E_i / E_t) \quad (1.2)$$

$$SE = 20 \log \ (B_i / B_t) \quad (1.3)$$

Whenever electromagnetic waves passes through a certain shield, it can be attenuates in the form of absorption (A), reflection (R) and multiple internal reflections (M). So shielding effectiveness is the sum of these three mechanisms. So

$$SE = A + R + M \quad (1.4)$$

Metals and plastic materials can be used for electromagnetic shielding. Metals are the good conductor of heat and electricity, so electromagnetic waves can be reflected, obserbed and transmitted through the metals. Metallic conductor connected with earth can be used in electronic equipments to eliminate heat and static charges produced inside the electronic equipment. Similarly metallic materials can be used in shielding of electronic components to protect it from electromagnetic radiation produced inside and outside environment [10]. The common metallic shielding materials are the combination of metals and its alloys, such as Nickel (79%), Iron (14%), Copper (5%) and Chromium (1.5%). Other metals used in shielding are Silver, Aluminum, Stainless steel and Brass etc.

Metals used in shielding have certain drawbacks. It suffers from low impact resistance, high density and rusty effect, which decreases the shielding effectiveness of metallic shield. Plastic and rubber are natural insulators and do not absorb or reflects electromagnetic waves. Different conductive filler such as metallic powder, ferrites, carbon black and graphite are added to plastic by different ways to achieve desired shielding properties in plastic.

- Metallic coating on plastic

The surface of plastic is coated with metals by the following coating technique for desired shielding of plastic [11-12].

- Conducting paint
- Electroplating
- Zinc arc spraying

Plastic materials are electrically insulator having resistivity in order of 10^{15}-10^{18} Ω cm. But plastic can be made conductive by adding different conductive filler including carbon black, Stainless steel fiber, Aluminum fiber and Nickel coated graphite fiber.

1.4.2: Carbon black / fiber

Carbon black can be used in rubber industry for enhancement of mechanical properties of goods and in plastic industry as conductive filler in cables. Carbon black is a semiconductor having resistivity in order of 20-0.5 Ωcm. However when carbon black is mixed with plastic and rubber, then the resulting compound gives conducting properties.

Luo and Chung [13] observed that the SE of continuous carbon fiber is better than discontinuous carbon fiber due to reflection losses. The reflection losses in continues carbon fiber are more than the discontinuous fiber due to better connectivity. Conductivity of high density polystyrene, when carbon fiber is mixed with carbon black at different concentration. Carbon black particle enhances the internal connectivity of fiber and provide a large conductive path for charge carriers. Conduction losses inside high density polyethylene increases due to large conductive path, which results high shielding effectiveness.

1.4.3: Stainless steel fiber

Steel fiber is mixed with nylon and poly phenylene oxide having shielding effectiveness 36-42 dB. Baker *et al.* [14] studied Shielding effectiveness of polymer matrix filled with stainless steel fiber. The dispersion of stainless fiber inside polymer composites act as a conductive mesh, and it can be used for shielding application. Other metallic fiber can also be used for shielding materials such as Aluminum, Iron, Copper and Brass.

1.4.4: Shielding of electronic devices by metals and plastics materials

Laptop in normal operation can emits low frequency electromagnetic radiation and heat from the base. These electromagnetic radiation and heat are harmful for human health.

Heat absorbed by the body can damage the body cells and cause cancer. While electromagnetic radiation can damage DNA cells. Different shielding materials are used to eliminate heat and electromagnetic radiation. Laptop tray can be used to eliminate electromagnetic radiation and heat. Laptop tray having metal surface can absorbs 99% electromagnetic radiations. Two cooling fans inside the tray can cool different parts of laptop and eliminate heat produce by laptop.

Cell phone can emits electromagnetic radiation in all direction up to 6m distance in the surrounding region. These radiations affect the performances of electronic equipments such as laptop, television and radio etc. While using cell phone near the head can causes brain cancer, headaches and defects in vision? Different shielding equipments can be used to eliminate electromagnetic radiation produced by cell phone, including pocket shield, Bluetooth and shielding cap.

Pocket shield is made from combination of metals and alloy, which consists of Nickel, Cobalt and Copper. It can deflect heat and electromagnetic radiation. Bluetooth can also be used to transmit sound signals to ears without harmful electromagnetic radiation to head. Shielding cap is made from combination of polyesters/cotton and stainless steel fiber. It can protect brain by reflecting electromagnetic radiation.

1.5: Composites

A composite is formed by the combination of two or more than two materials having different physical and chemicals properties, but gives a new material having desired properties. All composites are made from two basic elements, i.e. matrix and reinforced materials. Reinforced materials individually posses very weak physical properties, but when they are joined together by matrix then their physical properties such as compressive strength and tensile strength enhances[15].

Composites are basically two types.

1.5.1: Natural composites

Naturally occurring composites are found in plants and animals. Bones in animals are made from calcium phosphate and collagen. Calcium phosphate is hard but collagen is soft. When calcium phosphates are joined together by collagen, they form bone. These bones can perform different function in our bodies. Similarly wood is a composite made from cellulose and lignin. Cellulose itself is very weak, but when cellulose are joined together by lignin, it form wood which is very hard and strong.

1.5.2: Man-made composites

Early man made composites are bricks and concrete. Bricks are made from mud, which can easily be break but cannot be compressed. To increase its tensile strength, it is possible to make bricks from mud and straw. Similarly concrete as also a composite made from stone, cement and clay. Concrete have high compressive strength but weak tensile strength. Their tensile strength can be increased by using steel as a reinforced material in concrete.

Various composites are formed by filling metals, ceramic and polymer for desired tensile strength, compressive strength, young modules and resilience etc. On the basis of matrix composites are divided into three types.

- Metal matrix composites
- Ceramic matrix composites
- Polymer matrix composites

1.6: Literature review

1.6.1: Nanocomposites

Nanocomposite is formed by the combination of two or more than two different solid materials having particle size less than 100 nm. Nano materials are the combination of two different Phases. One phase is called filler having size in nanometer which the properties of new materials called reinforced materials. While other phase is called matrix. Matrix may be metal, ceramics or polymer [16].

The properties of nano materials depend on the properties of matrix and on the nanofiller conductivity, dispersion and distribution inside the matrix materials.

1.6.2: Classification of nanocomposites

Nanocomposites are classified into three types on the basis of matrix.

- Ceramics matrix nanocomposites
- Metals matrix nanocomposites
- Polymer matrix nanocomposites

1.6.2.1: Polymer matrix nanocomposites

Polymer nanocomposites are the materials made from inorganic discrete particles having size less than 100 nm dispersed in polymer matrix to enhance the properties of polymer [17]. The nanofiller which enhances the properties of polymeric nanocomposites are called reinforcing nanofiller.

The nanofiller, which I have used in my experiment is carbon nanofiber for the purpose of electromagnetic shielding.

1.6.2.2: Carbon nanofiber as filler

The physical properties of carbon nanofiber are different from multi walled carbon nano tube (MWCNTs). Carbon nanofiber are not in the form of concentric cylinder just similar to MWCNTs. The diameter of carbon nanofiber is small as compared to MWCNTs, which produces a large surface area in fiber [18] having aspect ratio larger than 100. Carbon nanofibers exist in the form of cone. But these cones are not arranged just like the concentric cylindrical tube of MWCNTs.

Al-Saleh and U. Sundararaj observed that vapor grown carbon nanofiber conductive polymer composites have brilliant shielding effectiveness and electric properties as compared to conductive polymer composites [19]. These electrical and thermal properties depend upon the nanofiber dispersion, division, peculation threshold and aspect ratio. Peculation threshold is the conductive path formed by the carbon nanofibers particles inside the conductive polymer. Fig. 1.2. shows that when CNFs particles agglomerated no conductivity occurs. Similarly in Fig. 1.3 and Fig. 1.4 there is no conductivity due to well dispersion but bed distribution of CNFs and well dispersion and division without inter connection of CNFs. Conductivity occurs only due to percolation threshold formed by CNFs particles inside the composites as shown an Fig. 1.5.

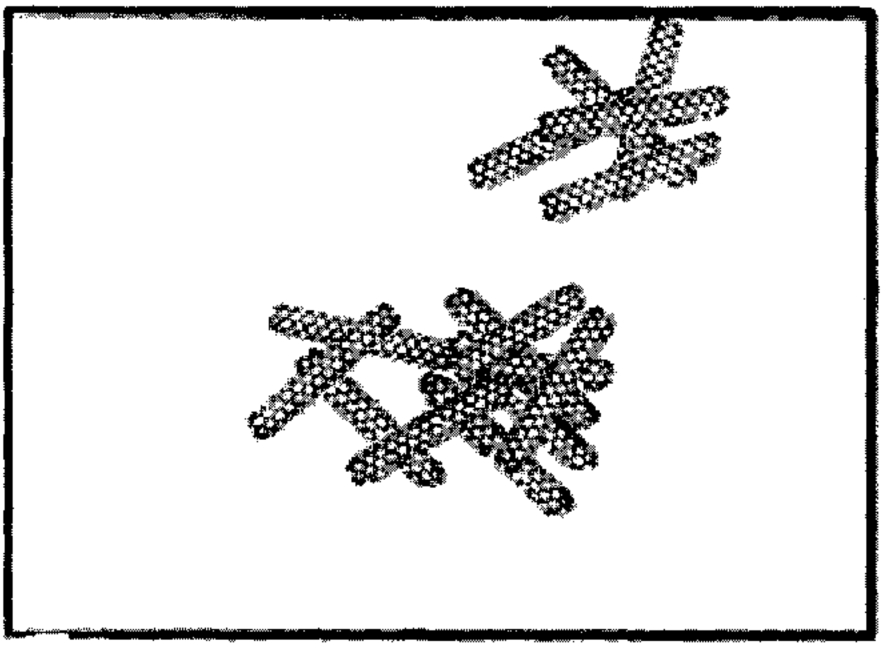

Fig. 1.2: *No conductivity due to bed carbon nanofibers dispersion and division [19].*

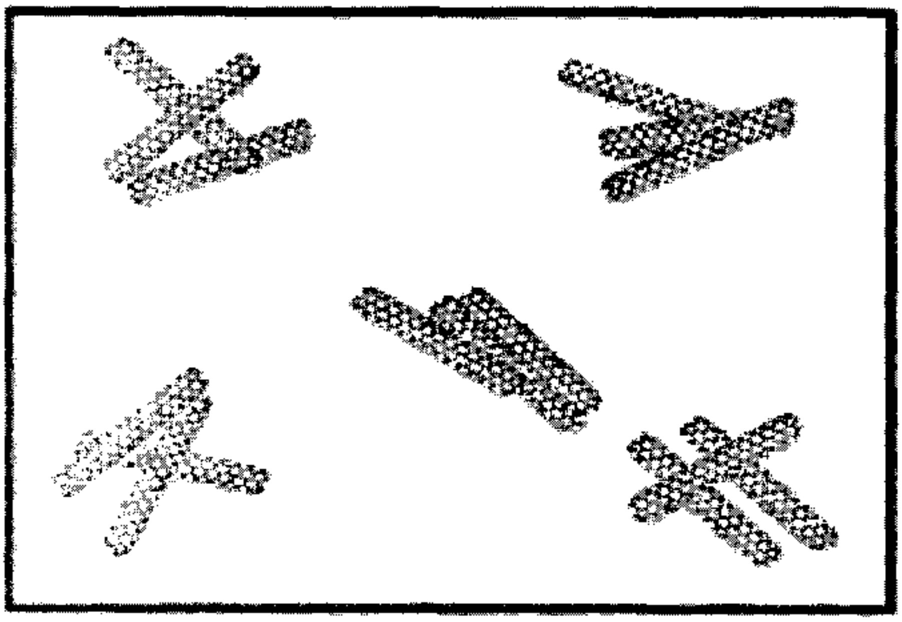

Fig. 1.3: *No conductivity due to carbon nanofibers well dispersion and bed division [19].*

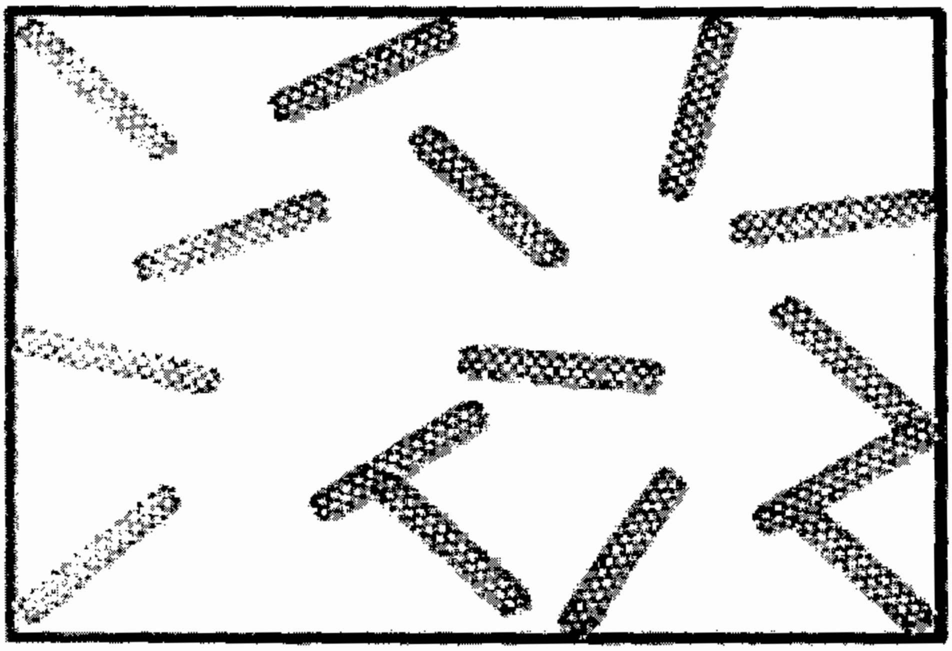

Fig. 1.4: *No conductivity due to carbon nanofibers well dispersion and division without inter connection [19].*

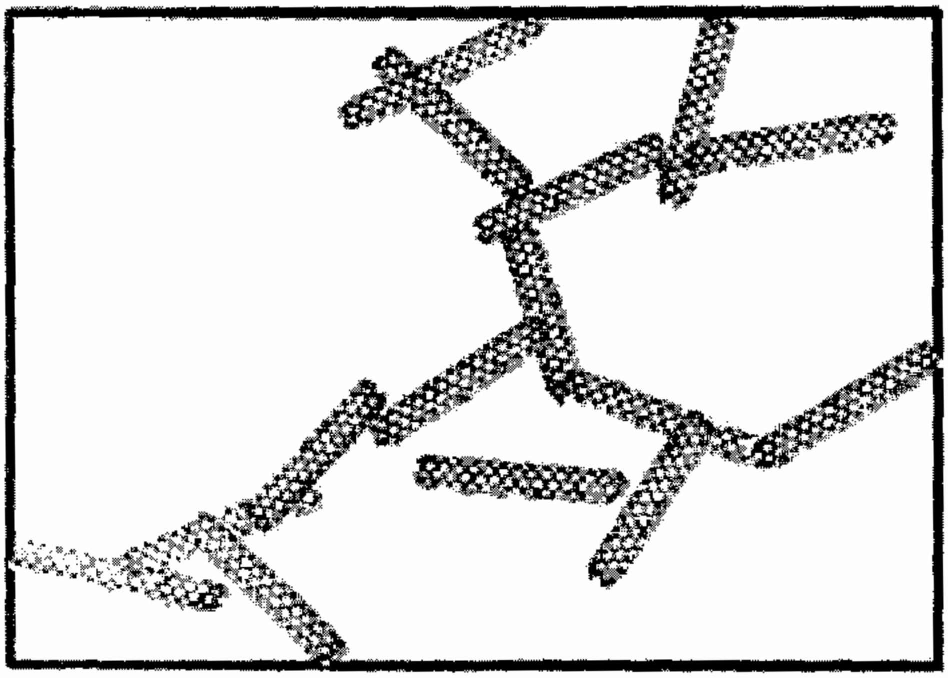

Fig. 1.5: *Conductivity due to carbon nanofibers well dispersion and inter connection but bed division [19].*

S. Yang and K. Lozano [20] studied the surface resistivity and shielding effect of vapor grown carbon nanofiber in liquid crystal polymer composites. When vapor grown carbon nanofiber were mixed with liquid crystal polymer, then the surface resistivity of liquid crystal polymer decreases 11 times from their original surface resistivity. But thermal conductivity of the composite shows no improvement with carbon nanofiber insertion. These nanocomposites shows shielding effect up to 41dB due to reflection and multiple reflections.

B. O. Lee and W. J. Woo [21] observed shielding effect and conductivity of carbon nanofiber coated with poly Vinylidene fluoride. They observe that shielding effect of carbon nanofiber is higher than other due to larger surface area and aspect ratio. The conductivity of coated carbon nanofiber increases from 1.34 to 1.91 S/cm, when thickness of coated carbon nanofiber is increased from 50-60 μm. However when carbon nanofiber was milled with ball mill, then both conductivity and shielding effect decreases due to agglomeration of carbon nanofibers and thus decreases percolation threshold. Fig. 1.6 shows, that conductivity of coated CNFs increases form 1.4 S/cm to 1.9 S/cm with increase in thickness from 25 microns to 100 micron.

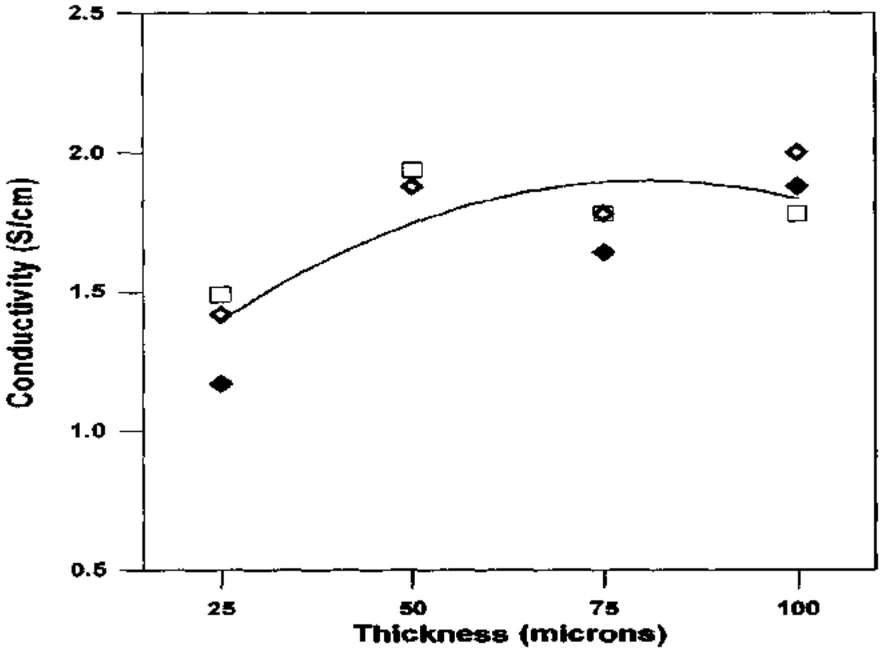

Fig. 1.6: *Conductivity increases with increase in thickness [21].*

Fig. 1.7 shows that shieding effect has been incresed from 4 dB to 12 dB due to mechanical mixing as compared to ball milling of carbon nanofibers.

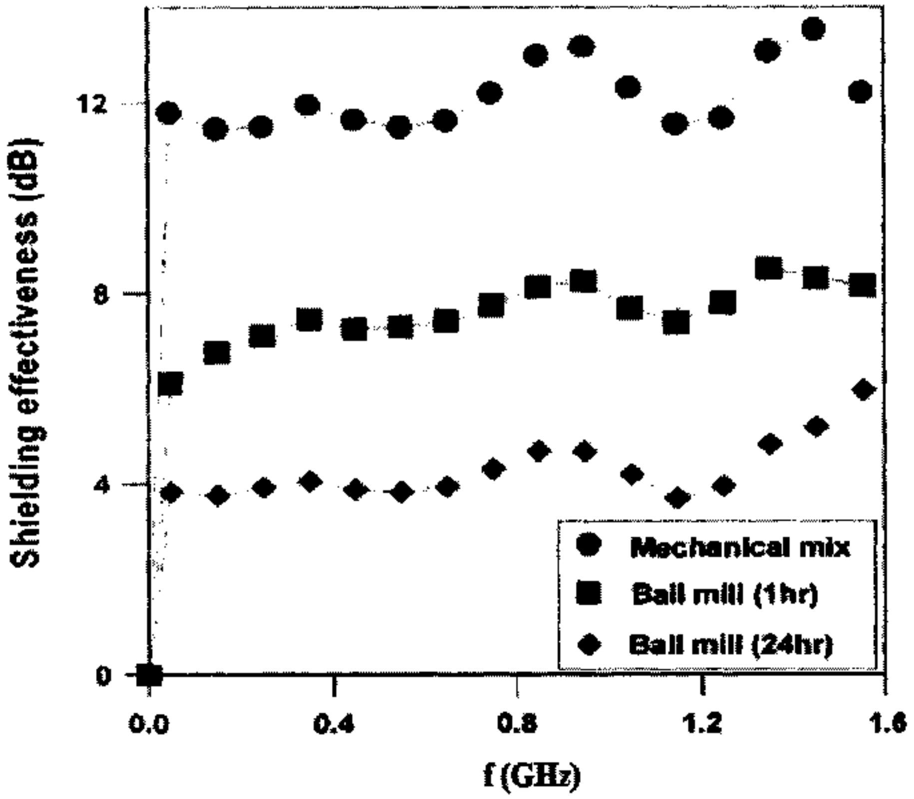

Fig. 1.7: *Shielding effect decreases due to milling of carbon nanofiber [21].*

Park *et al.* [22] build single layer mixed microwave absorbers' by using carbon nano fibers as a dielectric absorbing materials and NiFe particles as a magnetic absorbing materials. Their complex permittivity and permeability were measured in microwave frequency range from 2-18 GHz. Due to thinner thickness RAMs shows better absorbing properties. Their maximum reflection loss becomes 10 dB at the thickness of 2.00 mm in X-band along with the thickness of 1.49 mm with frequency in Ku-band. Fig. 1.8 shows single layer microwave absorber used for microwave absorption placed at quarter wavelength separation from conducting material.

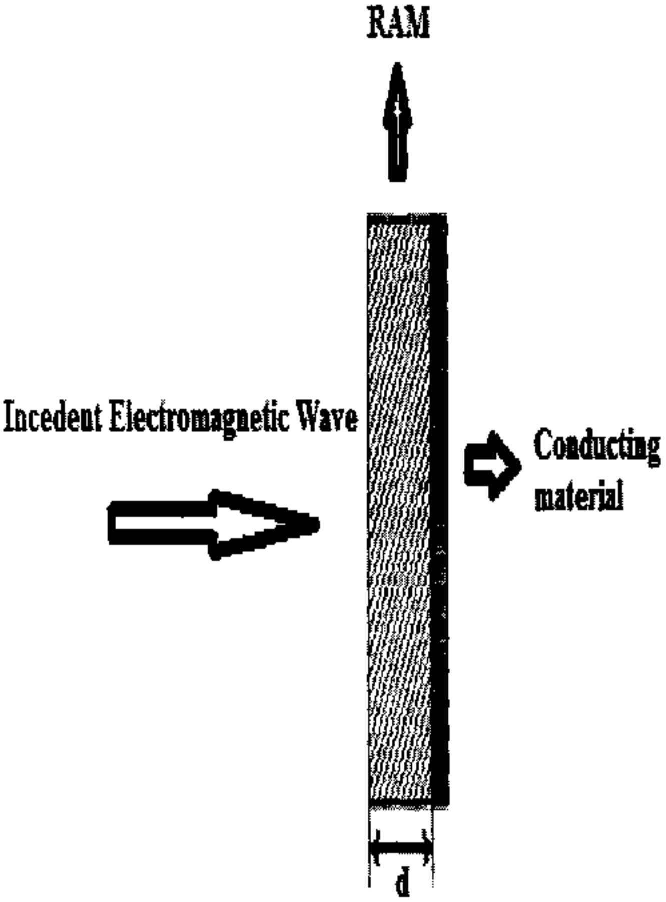

Fig. 1.8: *Single layer microwave absorber [22].*

G .G. Tibbett's and M. L. Lake [23] studied the tensile strength and electrical conductivity of vapor grown carbon nanofiber with polymer composites. The fabrication of these nanocomposites requires a special care due to strong bonding between the fibers. If these nanocomposites are prepared carefully, then their tensile strength increases three times more than the polymer composites with 15% of fiber volume inclusion. But at the same time conductivity of fiber composites decreases due to 15% fiber volume loading. It can also be increased by careful preparation of 0.5% of fiber loading.

B. O. Lee and W. J. Woo [24] observed the shielding effect and electrical conductivity of carbon nanofiber in polymer matrix composites. Nanofibers were mixed in poly vinyl alcohol (PVA). Their electrical conductivity increases from 0.033 to 0.169 S/cm which depends strongly on catalytic composition of carbon nanofiber. When carbon nanofiber were heated at 1100^0 C temperature, than shielding effect increases from 1.6 to 4.8 dB as shown in Fig. 1.9.

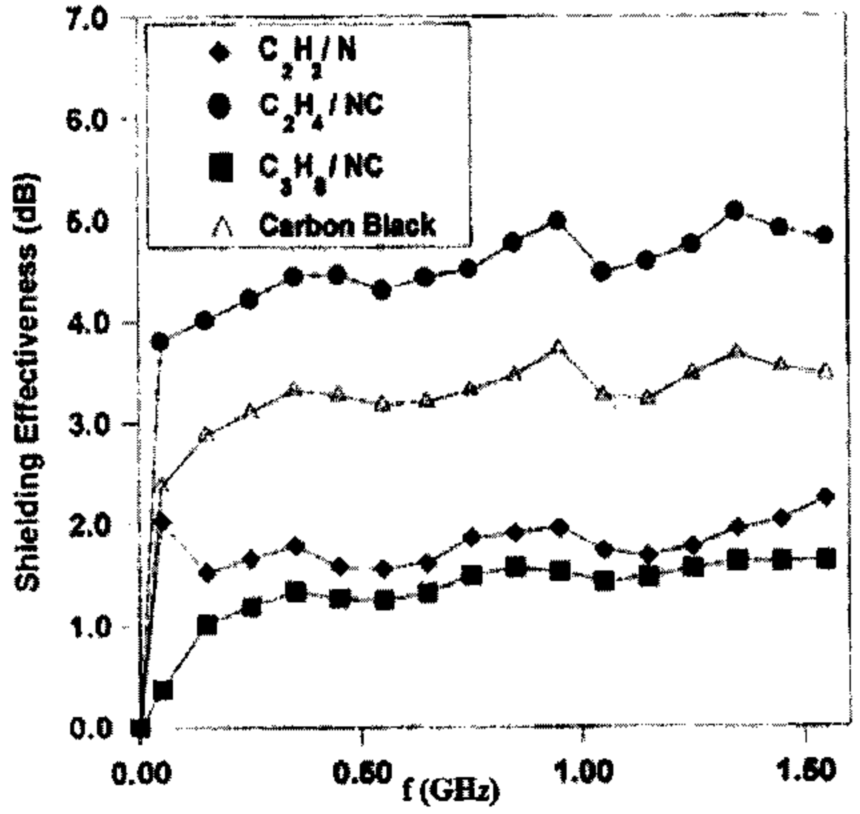

Fig. 1.9: *Shielding effect increases with carbon nanofibers and carbon black filled with PVA at heating [24].*

K. H. Wong and S. J. Pickering [25] observed the shielding effect of recycled carbon fiber composites. Recycle carbon fiber was converted to non-woven Viel by using fluided bed technique into desired shape of glass fiber polymer planes. They observed that shielding effect increases with increase in area of veil but it is independent of separation of fibers inside the composites. Thus shielding effect increases from 40 dB to 70 dB, when glass fiber plane was placed inside the two planes of Recycled fiber veil.

L. V. Xiao and J. Jin [26] studied complex permittivity, permeability and reflection losses of carbon nanofiber in X-band frequency. These nanofibers were prepared by wet-spinning method from polymer mixed with polyacrylonitrile and polymethyl methacrylate.

X-ray diffraction spectroscopy and Raman spectroscopy were used to study the carbon blend structure. Reflection losses were studied at different thickness of single layered absorber backed by perfect conducting plane at 8wt% of carbon nanofiber loading. It was observed that the reflection loss becomes -34 dB at 10.5 GHz frequency at a thickness of 2.1 mm as shown in Fig. 1.10.

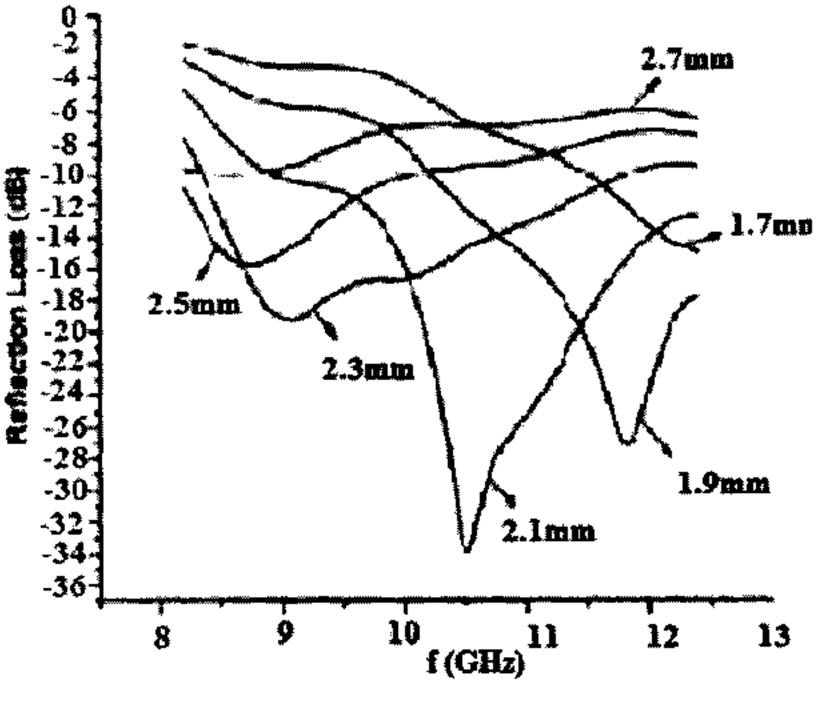

Fig. 1.10: *Reflection losses of composite containing 8wt% CNFs with different sample thickness[26].*

A. linear and has co-workers [27] observed that the conductivity of carbon nanofibers and polyamide 6, 6 nanocomposites. They prepare these nanocomposites by compression molding and compare their electrical conductivity with melt mixing method. It has been observed that conductivity of carbon nanofiber polyamide composites was better than those prepared by melt mixing. These observations were carried out at different grain size ratio of polymer to carbon nanofiber.

S. Kumar and his company [28] fabricated Syndiotactic polystyrene/carbon nanofiber composites by compression molding and study their electrical and thermal properties. Scanning electron microscope was used to examine the surface morphologies of these composites. X-ray diffraction technique was used to study the alignment of carbon nanofiber and polymer. The resistivity decreases with increase of carbon nanofiber weight fraction. Their electrical and thermal property enhances by mixing liquid crystalline polymer with syndiotactic polymer/carbon nanofiber composites. This enhancement is due to rigid molecular structure of liquid crystal polymer.

Li *at el.* [29] fabracated carbon nanofiber and porous carbonfiber by mixing polyacrylonitrile/polymethyl mathacrylate at a weight ratio of 70/30 and 30/70 with carbon. Two different types of composites were prepsared by mixing carbon nanofiber and porous carbonfiber in epoxy resin at 2-6 weight fraction . It was observed that composites having pours carbon fiber have better microwave obsorption than carbon fiber composites. The minimum reflection loss of porous carbon fiber becomes -31dB at 9.7 GHz, while the compositses having carbonfiber have reflection loss -12.2 dB at 10.7 GHz. The maximum obsorption in porous carbon fiber is due to interference of multiple reflection and dielectric constant. Fig. 1.11 shows absosorption losses of CNFs composites with a thickness of 3 mm.

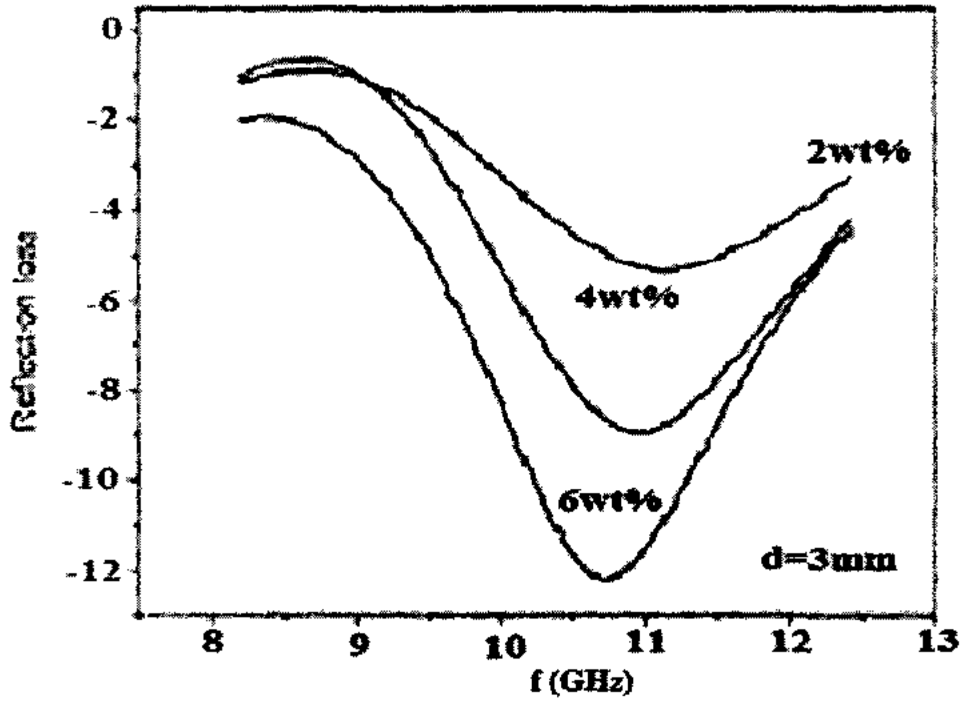

Fig. 1.11: *Absorption properties of composites filled with CNFs with a thickness of 3mm [29].*

Fig. 1.12 shows that absorption loss in CNFs 6wt% composites is larger as compared to 2wt% and 4wt% CNFs composites having same thickness of 2.3 mm. Maximum reflection loss occures is -30 dB at 8 GHz frequency.

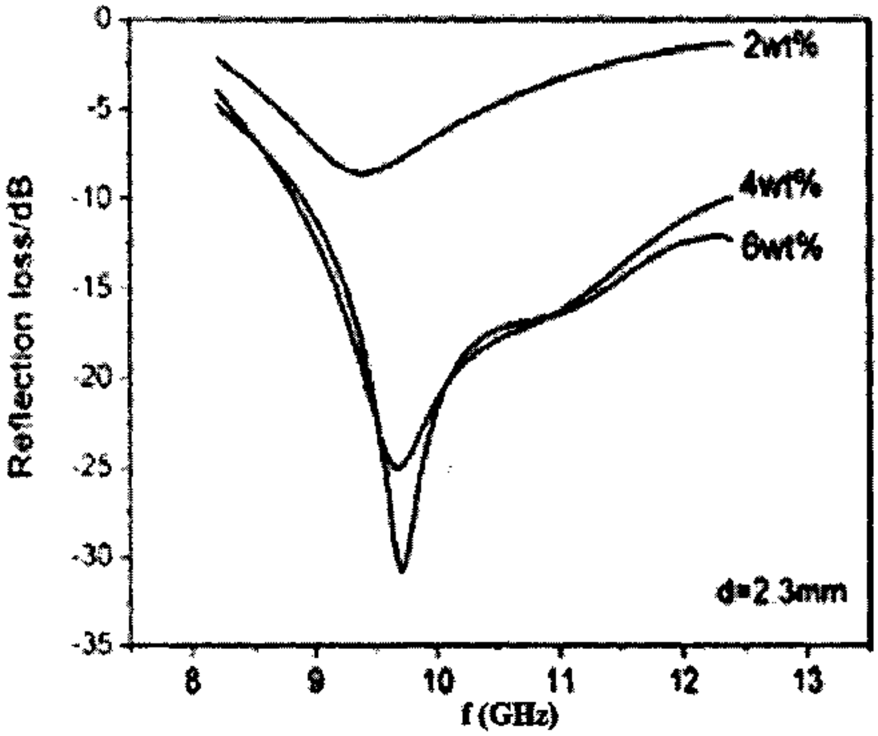

Fig. 1.12: *Absorption properties of composites filled with CNFs with a thickness of 2.3 mm [29].*

J. Geo *et al.* [30] studied the electrical and mechanical properties of graphite nano particles mixed with carbon nanofiber composites. These composites were prepared by ultrasonacator and electrospining process. It was observed that graphene nano particles were embedded on the surface of nanofiber only, when size of graphene becomes equal to the diameter of nanofiber. X-ray diffraction technique reveals that sonication has no effect on the spacing layers of carbon nanofiber. Raman spectroscopy shows that the interaction between graphene nano particles and polyurethane nanofiber. These nanocomposites shows better hardness and electrical properties as compared carbon nanofiber polymer matrix composites due to will dispersion and strong interaction of graphene nanoplatelts on the surface of carbon nanofiber. During sonication process cavitations bubbles were created inside the liquid solution, which vibrate during compression and rarefaction. The size of bubble decreases during compression, but increases during rarefaction. When size of bubble becomes equal to twice of their original size, it that time bubble collapse and produces shock waves. These shock waves ignite particles inside the liquid solution and pushes graphene nano particles towards the carbon nanofiber. Graphene nano particles stuck with the surface of nanofiber. Due to better percolation threshold electrical conductivity enhances.

1.7: Dielectrics

Dielectrics are any insulting material which stores electric energy in the form of electric field, if it were placed in capacitor. When dielectric material is placed in electric field, it does not produces current similar to the conductor, because it does not possess free charges, but the atoms of dielectric are separated through a small distance. Positive charged nucleus moves along the direction of field and electron opposite to the direction of field and produces electric field directing from positive charged nucleus toward the negative charged electron. This field will decrease the applied electric field [31].

1.7.1: Dielectric constant

Dielectric constant is the ratio of capacitance of capacitor, when dielectric medium is inserted to capacitance of capacitor, when medium is air or vacuum.

Mathematically it can be represented as

$$\acute{\varepsilon} = C/C_0 \qquad (1.5)$$

Where

$\acute{\varepsilon}$ = Dielectric constant

C = Capacitance of capacitor when dielectric medium is inserted

C_0 = Capacitance of capacitor when medium is air or vacuum

When dielectric medium is inserted between the charged parallel plate's capacitor then atoms of dielectric becomes polarized and produces internal electric field opposite to the external electric field, thus external field decreases and hence capacitance of capacitor increases. Fig. 1.13 shows polarization of dielectric medium placed between capacitor plates.

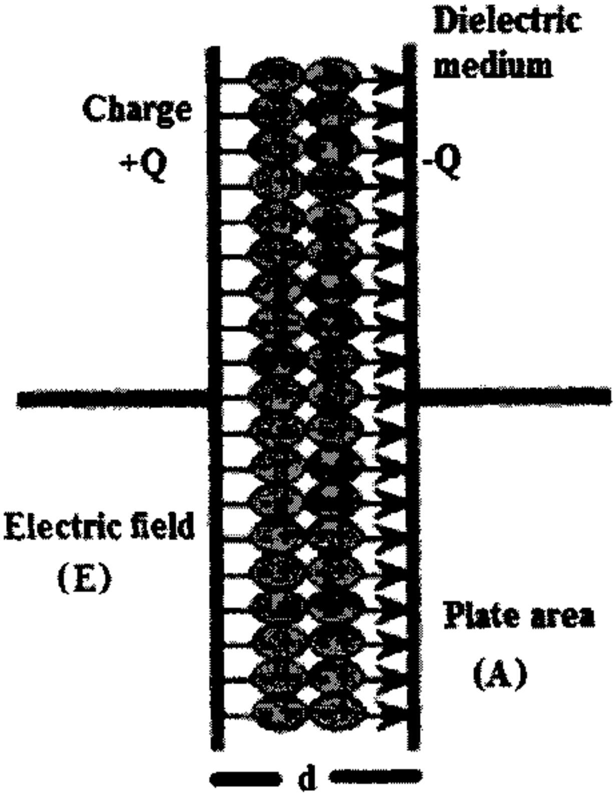

Fig. 1.13: *Polarization of dielectric medium placed between parallel plate capacitor [31].*

Mathematically when dielectric medium is inserted between capacitor plates, then the capacitance of capacitor becomes

$$C = \frac{A\varepsilon}{d} \tag{1.6}$$

Where A = Area of the plates

ε = Permittivity of dielectric medium

d = Separation between the plates

When capacitor are placed in air or vacuum, then capacitance of capacitor becomes

$$C_0 = A\varepsilon_0/d \tag{1.7}$$

Where C_0 = Capacitance of capacitor, when medium is air or vacuum

ε_0 = Permittivity of air or vacuum

Putting Eq. 1.7 in Eq. 1.5

$$\varepsilon' = Cd/A\varepsilon_0 \tag{1.8}$$

In our present work, we have prepared different kinds of carbon nanofibers absorbing sheets for electromagnetic waves absorption by mixing carbon nanofiber in epoxy resin (5052) by solution process technique. So epoxy resin between the carbon nanofibers grains act as insulating medium. So carbon nanofibers along with epoxy resin in composite sheets forms mane-capacitor and stores electric energy in the form of electric field.

1.8: Polarization

Polarization is the separation of positive and negative charges on the face of dielectric medium due to applied electric field.

Mathematically

$$\mathrm{P} = \text{sum of } \mathrm{p}/\mathrm{v} \tag{1.9}$$

Where

P = Polarization of medium

V = Volume

Dipole moment is directed from negative to positive charge.

1.8.1: Types of polarization

There are three types of polarization.

- Atomic polarization
- Interfacial polarization
- Dipolar polarization

1.8.1.1: Atomic polarization

When a dielectric material is placed in external electric field, then atoms of dielectric becomes polarized and positive charged nucleus and negative charged electron are separated by small distance and produces dipole moment from negative to positive charge, such type of polarization is known atomic polarization. The induced dipole moment (p) exist is long as electric field exist. Wherever electric field is removed, then dipole moment will vanish. Fig. 1.14 shows a natural atom of dielectric material, when external electric field is applied then atom of dielectric materials becomes polarized.

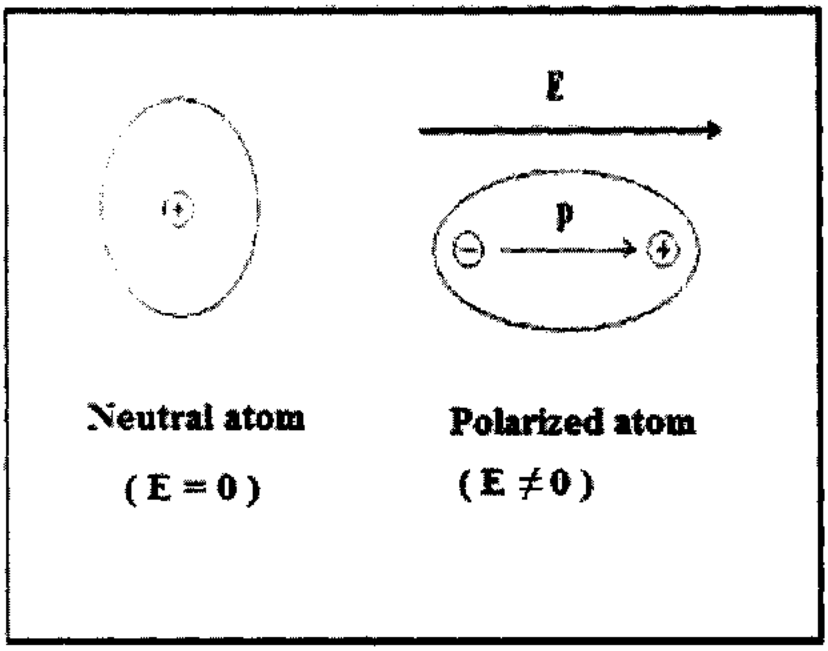

Fig. 1.14: *Polarization of atom of dielectric material due to applied electric field [32].*

1.8.1.2: Interfacial polarization

Interfacial polarization is produced due to the molecules of conducting and insulating grains boundaries. In carbon nanofibers composites, epoxy resin act as non-conducting grain boundaries. When electron reaches to epoxy resin boundary, they cannot cross it due high resistance of epoxy resin. These electron collected it one side and produces interfacial polarization.

1.8.1.3: Dipolar polarization

When uniform electric field is applied, then molecules experience a torque due to dipole moment and align along the direction of applied electric field, such type of polarization as known dipolar polarization. Fig. 1.15 shows dipolar moment of water molecule ($H_2 0$) due to uniform applied electric field.

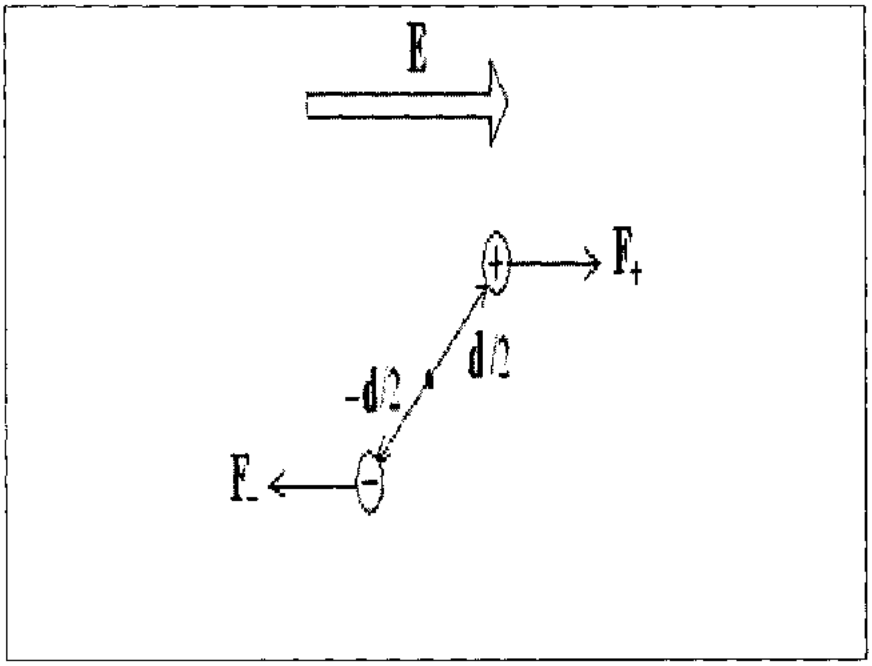

Fig. 1.15: *Dipole moment of water molecule due to applied electric field [31].*

1.9: Layout of the Thesis

Literature review suggests that different properties of electromagnetic shielding can be enhanced by varying different factors for better multilayer shielding in broad band. The objective of this work is to prepare nanocomposites sheets with a minimum thickness by filling conductive carbon nanofibers in epoxy resin. Incident electromagnetic waves will absorb inside the absorbing sheets in microwave frequency range from 11-18 GHz. So this work is about "Manufacturing of nanocomposites filled with carbon nanofibers for electromagnetic waves absorption" in microwave frequency range from 11-18 GHz.

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[31] En.wikipedia.org /wiki.org / wiki / Dielectric # Dipolar Polarization.

Chapter: 2

Synthesis of Nanocomposites

2.1: Materials

To prepare epoxy/glass fiber nanocomposites for electromagnetic shielding, carbon nanofibers were used as filler in epoxy resin. The objective was to see the electromagnetic shielding ability of carbon nanofibers. These carbon nano fibers were obtained from Chengdu organic chemical company LTD China. Epoxy resin (5052) was used as polymeric material in carbon nanofiber composites along with glass fiber and hardener (HY-5052) to prepare nanocomposites laminates.

2.1.1: Carbon nanofibers properties

In the present work of manufacturing nanocomposites for electromagnetic shielding, carbon nanofibers were used as filler in epoxy resin. Carbon nanofibers having 50 g weights has outer diameter 150-200 nm and length 10-30 um as shown in table 2.1. Carbon nanofibers having purity greater than 99%.

Table 2.1: *Different properties of carbon nanofibers.*

Properties	Carbon nanofibers
Weight	50 g
Length	10-30 um
Outer diameter	150-200 nm
Purity	>99%

2.1.2: Epoxy resin (5052)

Epoxy resins (5052) were used as matrix material in carbon nanofibers composites. Epoxy resin combines the composites together and protects the surface of glass fiber from harmful effects of environment. At normal temperature (25^0 C) epoxy resins (5052) have viscosity 1000-1500 mpa.sec and density as 0.94 g/cm^3 as shown in table 2.2.

Table 2.2: *Different properties of epoxy resin.*

Properties	Epoxy resin (5052)
Temperature	25^0 C
Viscosity	1000-1500 mpa.sec
Density	0.94 g/cm^3

2.1.3: Hardener (HY-5052)

Hardener (Hy-5052) was mixed in nanocomposites solution after sonication as a hardening agent. Hardener (HY-5052) at normal temperature (25^0 C) has viscosity 40-60 mpa.sec and density as 0.94 g/cm^3 as shown in table 2.3.

Table 2.3: *Different properties of hardener.*

Properties	Hardener (HY-5052)
Temperature	25^0 C
Viscosity	40-60 mpa.sec
Density	0.94 g/cm^3

2.2: Composites manufacturing techniques

Epoxy/glass fiber composites can be prepared by four different techniques.

- Hand layup technique,
- Vacuum bagging technique,
- Resin transfer molding (RTM) technique,
- Vacuum assistant resin transfer molding (VARTM) technique.

2.2.1: Hand lay-up technique

Composites used in aerospace technology can be prepared in desired shapes by open mold process known as hand lay-up coating method. Hand layup coating method is widely used in preparation of composites, because it is less expensive [1]. To prepare nanocomposites, several layers of glass fiber were cut. Epoxy resin and hardener were mixed in a beaker by mechanical stirrer. Now a single sheet of glass fiber was put in a tray and its surface was coated by epoxy resin with a brush. The surface of glass fiber was coated by a brush until it is completely wit. In a similar way all the layers of glass fiber ware coated one by one unless required thickness as achieved. Air trapped from inside the fabric can be removed by passing roller through the fabric [2-3] as shown in Fig. 2.1.

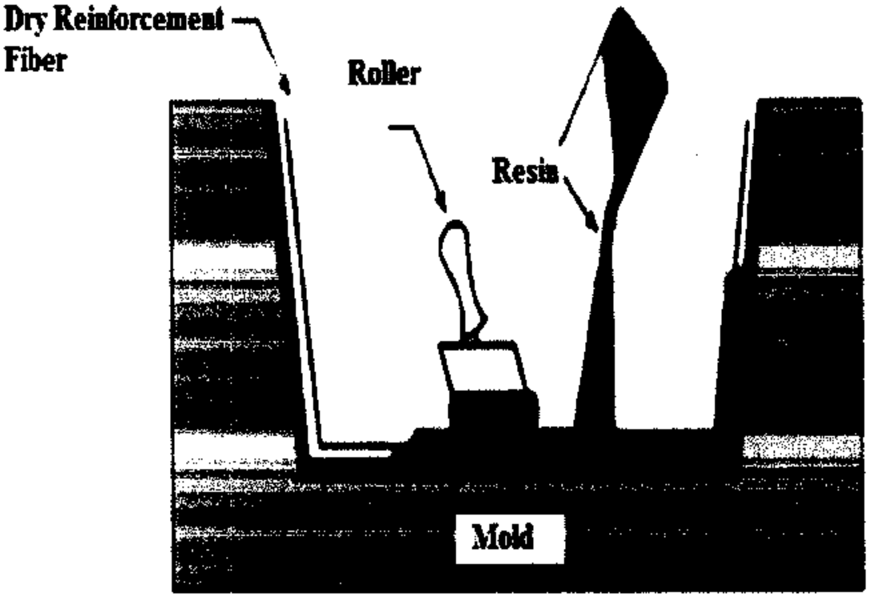

Fig. 2.1: *Structure of hand lay lap coating technique [4].*

Hand layup coating technique is simple and easily understandable, but it has a serious drawback due to open molding [4]. Air entrapped in fiber layers can produces vacant sites, which may result as cracks. These cracks decreases the strength of composite.

2.2.2: Vacuum bagging technique

Vacuum bagging technique consists of a vacuum pump which can remove air and creates vacuum inside the sealed vacuum bag, along with a coated composite laminates. This setup is kept under vacuum, because air entrapped can produces vacant site which may result cracks in the composite laminate[5]. First glass fiber layers are coated by composite solution by hand layup coated method, then coated composite laminates are placed on a glass mold. The whole sample was sealed with vacuum bag and vacuum is achieved by vacuum pump at -1bar pressure at 25^0 C temperature. The sample as remains under vacuum for 4 h. For further curing the sample remain left under vacuum for 24 h. After curing, the vacuum bag was removed and composite laminate ware placed in oven for further curing at 100^0 C temperature for further curing.

Vacuum bagging process have several advantages over hand layup coating process, some of them may be considered are

- Fiber layers are joined together strongly by vacuum bagging to form composites laminates for better mechanical properties.
- Vacant sites in vacuum bagging technique are less as compared to hand layup technique.
- Due to pressure difference fiber layers are bitterly wet out.

Vacuum bagging technique is more suitable then hand layup technique to produce high quality composites. Fig. 2.2 shows structure of vacuum bagging technique.

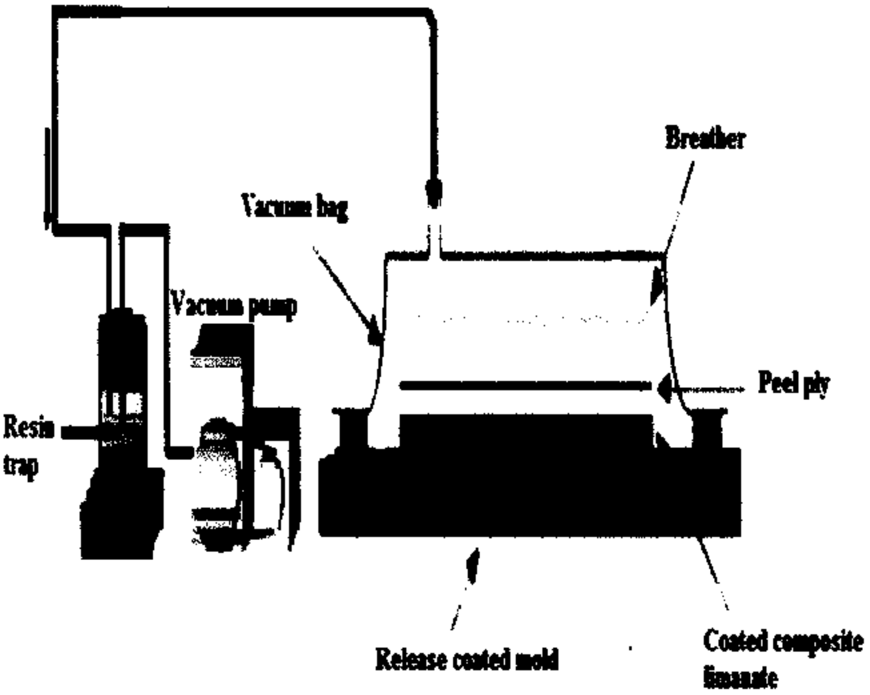

Fig. 2.2: *Composite sample cured by vacuum bagging techniqe [5].*

2.2.3: Resin transfer molding technique (RTM)

Composites can be prepared by closed mold process known as resin transfer molding process. In this method dry glass fibers were placed in a two sided metal mold [6]. Resin was transferred through the inlet port into the glass fiber sheets. On the other hand vacuum pump exerts pressure on outlet port due to which resin uniformly transfers through the fiber. When resin was completely passed through the fiber, then extra resin was extracted by the vacuum pump through the outlet port and stored in resin storage bottle [7]. When all the extra resin was extracted then vacuum pump was off after several hours and inlet and outlet port were sealed [8-9]. Fig. 2.3 shows transformation of epoxy resin through inlet port into glass fiber sheets by resin transfer molding technique.

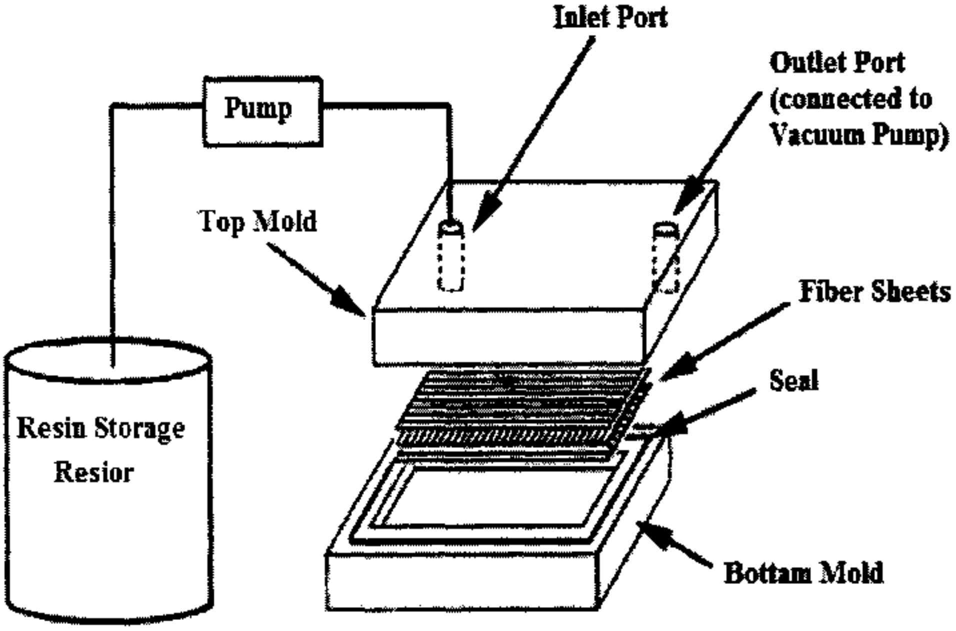

Fig. 2.3: *Transformation of resin through reinforced fiber by resin transfer molding technique [9].*

2.2.4: Vacuum assisted resin transfer molding technique (VARTM)

Resin transfer molding technique has been replaced by vacuum assistant resin transfer molding technique to reduce difficulties in design structure and cost associated with metal mold. In resin transfer molding process the upper half surface of mold is made from metal which is replaced by vacuum bag in vacuum assistant resin transfer molding process. In vacuum assistant resin transfer molding process first the vacuum pump is “on” to remove air and produces vacuum inside the mold. When all the air leaks have been removed present in vacuum bag, then -1bar pressure is achieved inside the mold [10] . Now epoxy resin was flown from outside in reinforcement medium. When epoxy resin completely wet the reinforcement medium, then extra resin was expel outside by vacuum pump and store in resin transfer bottle. Now inlet and outlet port are closed and vacuum pump was off. Then the reinforcement medium was remaining lift inside the mold to become cured for several hours [11].

Vacuum assistant resin transfer molding (VARTM) process has some advantages over resin transfer molding (RTM) process.

- At is widely used because it has low operating cost and requires short time.
- The upper half surface of the mold is made from vacuum bag instead of metal mold.

Vacuum assistant resin transfer molding process has a serious drawback.

- As vacuum bag is flexible, so the final thickness of the composites does not remain uniform.

Fig. 2.4 shows structural arrangement of VARTM technique.

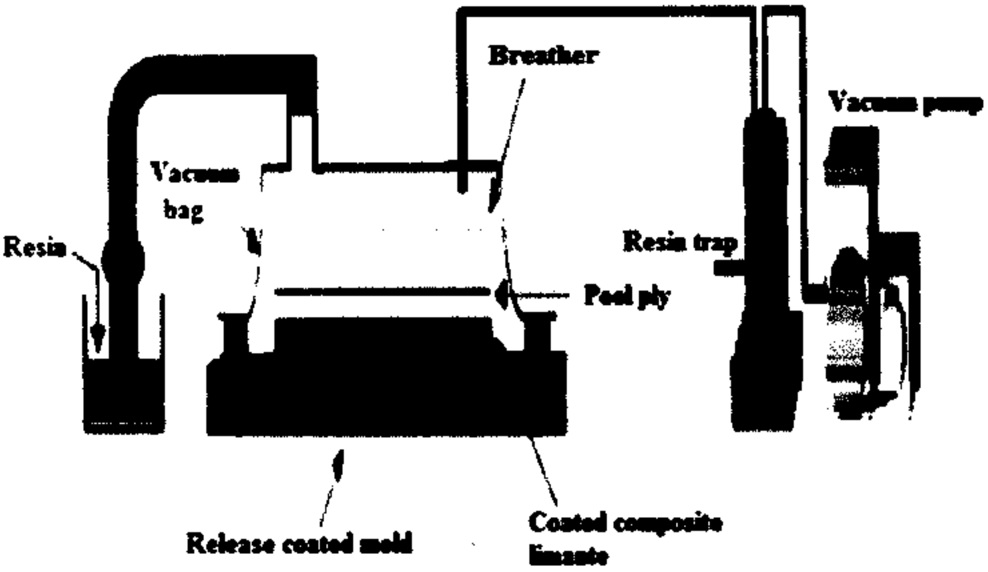

Fig. 2.4: *Resin flow through reinforcement medium by vacuum assistant resin transfer molding technique [5].*

2.3: Ultrasonacator

Ultrasonacator as a device which converts electrical signals into ultrasonic waves having frequency greater than 20 kHz, which can be used for dispersion of nano particles and degassing of air from a certain solution. Sonication is a process which is used for ignition of particles in a certain sample [12]. Fig. 2.5 shows sonication of nanocomposites by ultrasonacator.

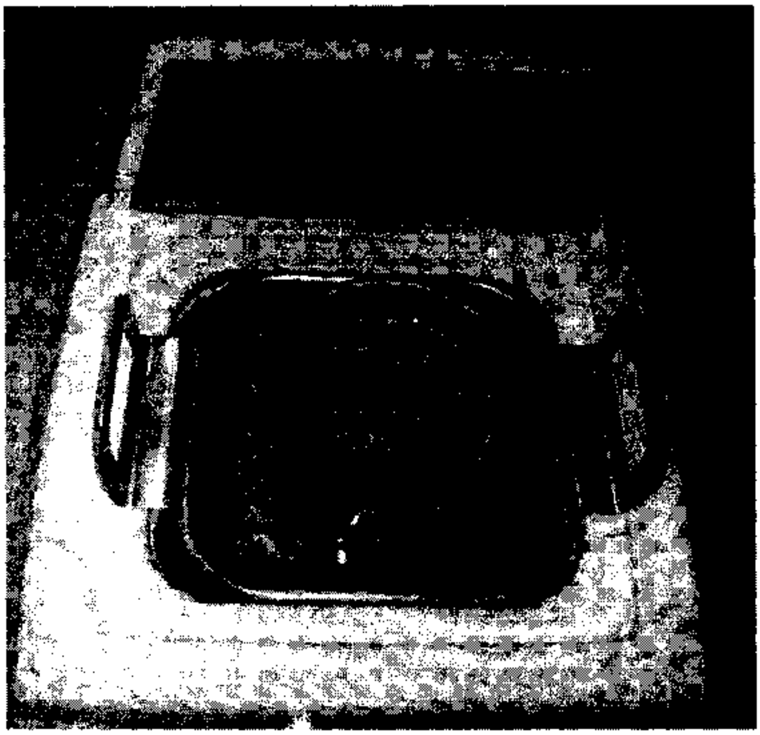

Fig. 2.5: *Sonication of nanocomposites by ultrasonacator.*

2.3.1: Working of ultrasonacator

Sonicator converts electrical signals into ultrasonic waves. These ultrasonic waves pass through the solution in the form of compression and rarefactions and molecules of liquid vibrates about their mean position [13] . During compression the molecules collapse one another while in rarefaction the average molecular distance of liquid increases. When the distance between the molecules becomes large enough as compared to the distance between them can contact one another. At that time liquid molecules break down and bubbles are created. These bubbles are known as cavitations. Bubbles are two types [14-15].

Stable bubbles are produced at low ultrasonic intensity from 1-3 W/cm^2, while transient bubbles are produced at high ultrasonic intensities up to 10 W/cm^2. When ultrasonic cycles in form compression and refraction passes through transient bubble, then the size of bubble increases, when size of bubble becomes twice to their original size, at that time bubble burst and emit energy in form of shock waves. These shock waves ignite particles inside the liquid solution. Fig. 2.2 shows shock waves produced due to burst of transit bubble.

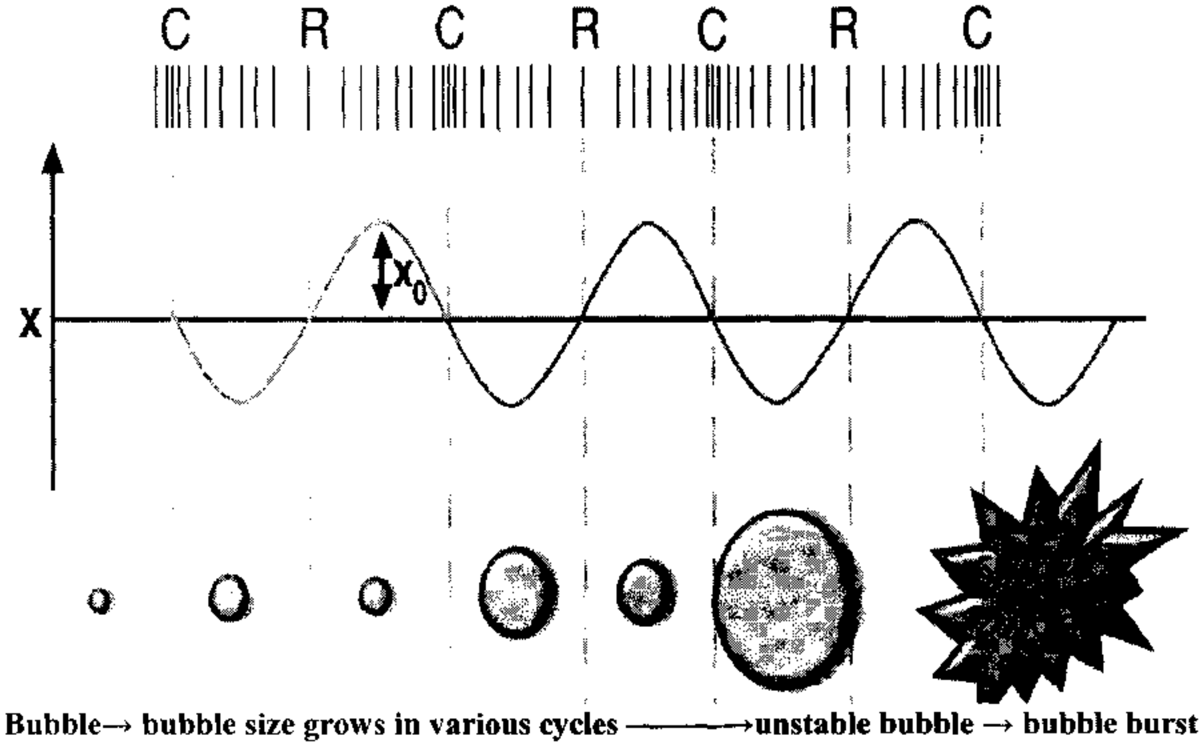

Fig. 2.6: *Shock waves produced due to burst of transit bubble[13].*

2.3.2: Application of ultrasonacator

It is used for two main purposes in laboratory.

- Degassing of air from a certain solutions.
- Sonication of nano particles.

2.4: Composites preparation

Two types of carbon nanofibers composites were prepared for electromagnetic shielding, i.e. thick carbon nanofibers samples and thin carbon nanofibers samples. Both samples were prepared by two different methods to observe different mechanism of electromagnetic waves.

2.4.1: Thin carbon nanofibers sample by vacuum bagging technique

Thin carbon nanofibers sample were prepared by vacuum compression and hand layup coating method. In each sample, 20 g epoxy resin (5052) was mixed with required carbon nanofibers weight percent measured by weight balance in a beaker. Then 10 ml ethanol was mixed in composite solution and stirred for 10 minutes by mechanical stirrer. Then composites solution was placed in ultrasonic bath for 45 minutes at room temperature. After sanction the sample was cold for 20 minutes. Then 38 wt% (7.6 g) hardener was mixed with composite solution and stirred by mechanical stirrer. Five layers of glass fiber were cut for sample preparation having size (6x6 inch^2). Single layer of glass fiber was put in a tray and was coated by composite solution with help of a brush. So all the layers were coated by the similar way until they were completely wet and superimpose one another. The glass mold was coated with poly vinyl alcohol (PVA) and cured for 45 minutes. After curing, the sample is placed on glass mold. Pal ply was placed on the top of sample and breather on the top of pal ply. The whole sample was sealed with vacuum bag. Then vacuum was achieved at -1bar pressure by vacuum pump for 1h. After 1h vacuum bagging, the vacuum pump was switched "off " and sample was remained left for 24 h under vacuum. Then sample was placed in an oven for further curing at 100^0 C for 4 h.

2.4.2: Thick carbon nanofibers sample by vacuum assisted resin transfer molding technique

Thick carbon nanofibers sample were prepared by vacuum assisted resin transfer molding technique and hand lay-up coating method. In each sample 20 g epoxy resin (5052) and carbon nanofibers required weight percent measured by weight balance were mixed together by mechanical stirrer in a beaker. 10 ml ethanol was mixed in composite solution to decrease the viscosity of solution. Then the composite solution is placed in ultrasonic bath for 45 minutes sonication at 65^0 C temperatures. After sonication the composite solution was cold for 15 minutes. Then 7.6 g hardeners (5052) were mixed in composite solution by mechanical stirrer for 5 minutes. Eight layers of glass fiber were cut for samples preparation having size (8x8 inch^2). Single layer of glass fiber was put in a tray and was coated by the composite solution with the help of a brush. Similarly all the glass fiber layers ware coated one by one in the tray. All the layers were coated by equal solution until they are completely wet and superimpose one another.

The glass mold was cleaned and poly vinyl alcohol (PVA) was coated on the surface of glass mold as a releasing agent. After 45 minutes curing, sample was placed in glass mold. Pal ply ware placed on the top of carbon nanofiber laminates and breather on top of pal ply. Breather was used to absorb the extra epoxy. The whole sample was sealed by vacuum bag for vacuum bagging. Two connectors were connected on the two sides of sample, one for vacuum bagging pipe and other one for pipe of epoxy flow. 45 g epoxy resin (5052) was mixed with 17.1 g hardener (5052) in a beaker measured by weight balance. Epoxy solution (epoxy + hardener) was degassed in ultrasonic bath for 5 minutes. Then vacuum pump was switched "on" to achieve vacuum at -1bar pressure. When vacuum was achieved then epoxy was flown by vacuum pipe. When epoxy was completely passed through the sample, then extra epoxy were extracted by vacuum pump, and vacuum pump was switched "off" after 1 h. The sample was cured in vacuum bag for 24 h. After 24 h the sample was placed in an oven for 4 h for further curing at 100^0 C.

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Chapter: 3

Characterization Techniques

Epoxy/glass fiber nanocomposites filled with carbon nanofibers were prepared for electromagnetic wave absorption. Four probes method and free space technique were used to measure dc electrical conductivity, complex permittivity and reflection losses of nanocomposites sheets. These two technique may be discussed in details. SEM ware also used to study the surface morphology of absorbing sheets.

3.1: Electrical resistivity measurement

The electrical resistivity of any material can be determined by using four probe method. Four probes method were first introduced by Winner in 1916 to find out the resistivity of earth [1]. In 1916 Valdes uses this method to measure the resistivity of semiconductor. It is also known as source measuring unit (SMU). It consists of four probes. Current I is applied to the two outer electrodes [2], while the resulting potential difference V is applied to the two inner electrodes. According to Ohm's law, potential difference V is directly proportional to the current I, if physical state of conductor remains constant.

$$V \propto I$$

$$V = IR$$

$$R = V/_I \qquad (3.1)$$

Where ''R'' is the resistance of conductor. The unit of resistance is ohm (Ω). The resistance R can be easily be measured by knowing the value of current I and potential difference V. At a constant temperature, the resistance R of conductor is directly proportional to length L but inversely proportional to the cross-sectional area A of conductor,

mathematically

$$R \propto L \qquad (3.2)$$

$$R \propto {}^{1}/_{A} \qquad (3.3)$$

By combining Eq. 3.2 and Eq. 3.3, we have

$$R \propto L/A \qquad (3.4)$$

Or $$R = \rho L/A$$

$$\rho = R A/L \qquad (3.5)$$

Where ρ (rho) in Eq. 3.5 represents resistivity of the composite sample. Resistivity is measured in ohm. meter (Ω.m). Also,

$$Area = width \times thickness$$

$$A = w \times t \qquad (3.6)$$

So Eq. 3.5 can be written as,

$$\rho = R \times {}^{(w \times t)}/_{L} \qquad (3.7)$$

The reciprocal of resistivity is known as conductivity. Conductivity measure the passage of current through any materials,

$$\delta = {}^{1}/_{\rho} \qquad (3.8)$$

Conductivity (δ) as measured in Siemens/meter$\left({}^{S}/_{m}\right)$.

Resistivity of any material can be find by two methods by using source measured unit (SMU).

3.1.1: Two probe method

Two probe method are useful for measuring resistivity of those samples having high resistance of 1MΩ and uniform cross-section area.

Let a specimen, whose resistivity is to be measured have uniform cross-section area A and length L. Two probes 1 and 2 are connected across the two ends of specimen [3] as shown in Fig. 3.1. DC source supplies a constant current I across the two ends of specimen, while the resulting potential difference V is measure by voltmeter connected in parallel with specimen. By knowing the value of current I, potential difference V, length L and area A of the specimen, the resistivity of the sample can be measured as

$$\rho = R \times \; w \times {}^{t}/_{\mathrm{L}} \tag{3.9}$$

Put $R = {}^{V}/_{I}$, then Eq. 3.9 can be written as

$$\rho = {}^{V}/_{I} \; \times \; w \times t/L \tag{3.10}$$

By putting the values, Eq. 3.10 gives the resistivity of specimen. Fig. 3.1 shows resistivity measurement of specimen by two probe method.

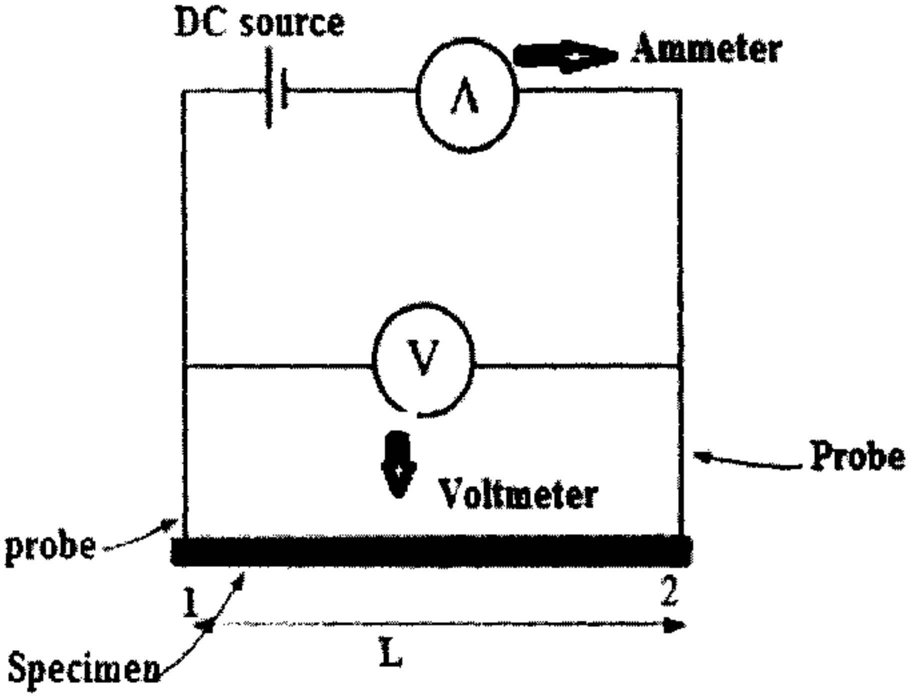

Fig. 3.1: *Resistivity of specimen by two probe method [3].*

3.1.1.1: Drawbacks of two probe method

- Two probe method can't be used for measuring resistivity of random shapes materials.

- Error in resistivity may occur due to the resistance of measuring probes.

Two remove these drawbacks, four probe method as used.

3.1.2: Four probe method

Four probe method are used to measure the resistivity of low resistance materials, because the resistance of measuring probes is equal to the resistance of materials. Four probe method consists of four tungsten metal tips having equal probe spacing of 1 mm. These metal tips can be moved up and down with help of a spring. A dc power supply is used to supply current to the two outer electrodes, while a high impedance voltmeter is connected in parallel across the two inner electrodes to measure potential difference. By measuring the current and voltage, the resistivity of low resistive specimen can be measured by four probe method. Fig. 3.2 shows resistivity measurement by four probe method.

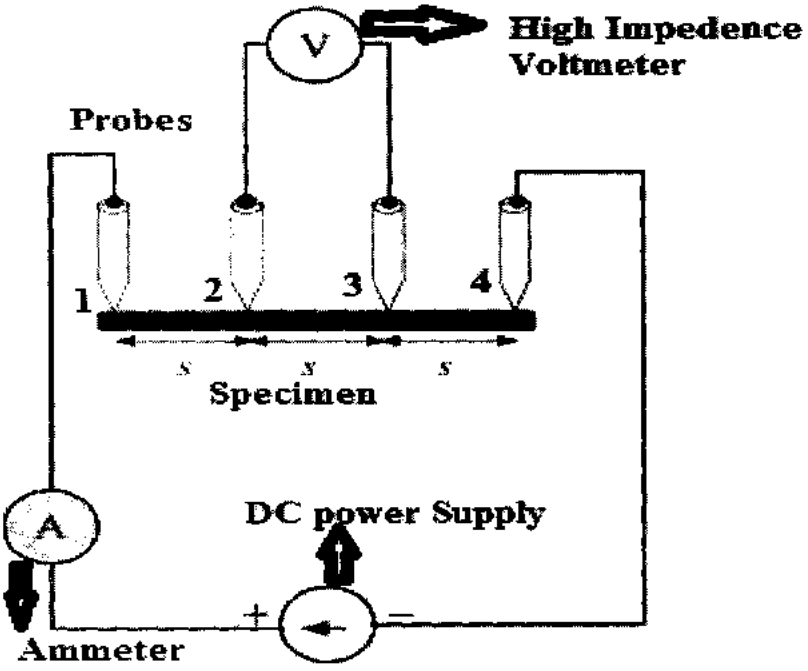

Fig. 3.2: *Resistivity of specimen by four probe method [3].*

3.1.3: Application of SMU

Source measurement unit (SMU) can be used to find out the resistivity of P-type and N-type semiconductor, ceramics, composites, solar cell, magnetic material and thin sheets. It can also be used for measurement of I-V curve of different materials.

3.1.4: Conductivity of CNFs sample by four probe method

Four probe method were used to measure the conductivity of carbon nanofibers sample. Four copper wires ware connected on surface of carbon nanofiber sample with the help of Silver past having equal spacing of 1cm as shown. Current is passed through the two outer probes, while the corresponding potential difference is measured by two inner probes. To find the resistivity of carbon nanofiber sample, first slope of I-V curve was taken and then thickness and width of carbon nanofiber sample was measured by Vernier caliper. Conductivity can be measured by taking the reciprocal of resistivity. Fig. 3.3 shows resistivity of CNFs absorbing sheet by four probe method.

$$\delta = \frac{1}{\rho} \tag{3.11}$$

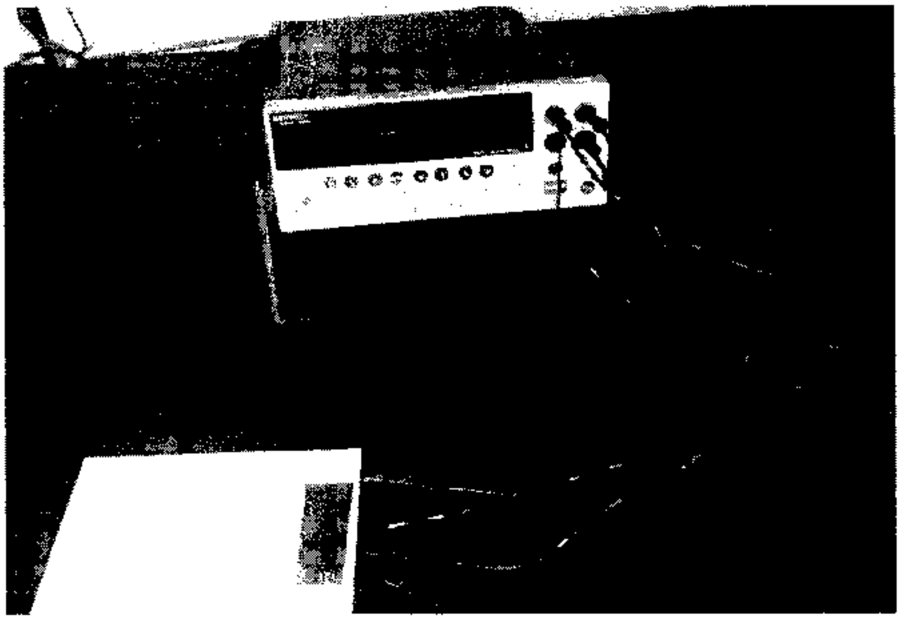

Fig. 3.3: *Resistivity measurement by four probe method.*

3.2: Microwave absorption

Absorbers are the flat materials that can obserbs energy and reduces the unwanted radiation that can degrate the operation of electranic equipment. Absorbers can be used inside and outside the system. It can be used inside the system to decrease oscilation produced by resonance and outside the system to eleminate reflection and transmation of signels to a particular object. Different techniques ware used to measure the reflection and transmation losses of these obsorber [4]. Free space technique as widley used to measure the reflection and transmition of these obserbers, which may be discussed in detail.

3.2.1: Free space technique

Free space technique is used to measure the electrical properties such as obsorption, transmation, real and imginary permitivities of obsorbing materials in microwave frequency range [5-6]. The shielding effect of a large flat sample can be determined by free space method from 1-18 GHz frequency range. This method consists of two horn antenna placed inside anechoic chamber. One horn antenna known as source antenna is connected with signal generator, while other one known as receiving antenna is connected with spectrum analyzer placed outside the anechoic chamber [7]. A small opening is left in the wall of shielding encloser just at the front of receiving antenna for sample adjusment. A large flat sample is fitted in opening along with metal plate having aperature size equall to the opening of shielding enclosure, so that electromagnetic waves can not leak out between the wall and sample. Fig. 3.4 shows structural arrangment of free space technique with a sample fitted in the wall of anechoic chamber betweem souce antenne and receiving antenna.

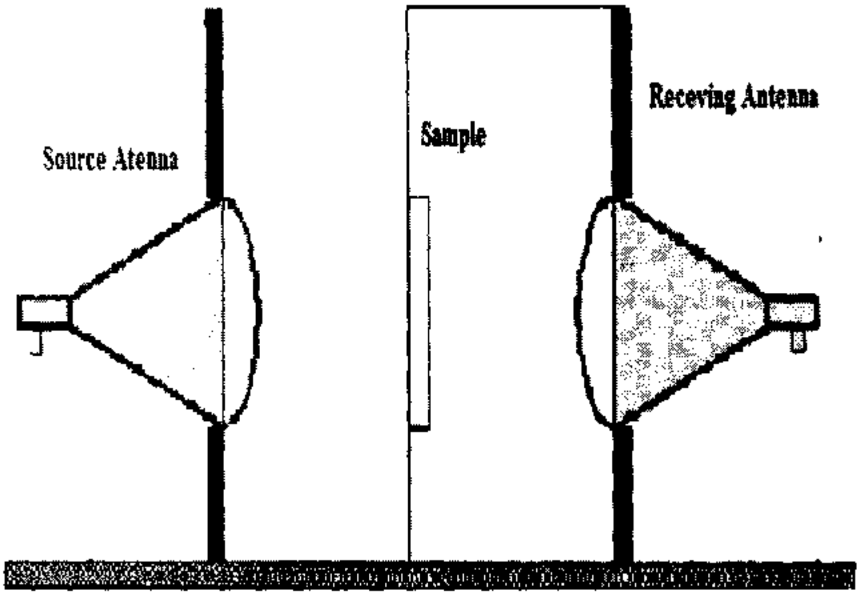

Fig. 3.4: *Structural arrangment of free space technique[8].*

Electromagnetic waves of certain required frequency ware incident on sample from source antenna.Two types of measurement were taken to measure shielding effect.

- Reference measurement
- Load measurement

Referance measurement E_1 is taken by measuring the incident electromagnetic waves emitted by source antenna.when their was no sample at the sample holder. On the other hand, load measurement E_2 is taken by measuring electromagnetic waves incident on the sample. During both measurement, Source and receiving antennas must be kept at the same position. So shielding effectiveness can be mathemeticaly expressed as

$$SE = 20 \log (E_1 / E_2) \quad (3.12)$$

Where

$$SE = SE_R + SE_T - SE_M \quad (3.13)$$

Where E_1 and E_2 represents reference and load field strength respectivily. The anechoic chamber was cleaned after each measurement with dry nitrogen to elemenate the sharpe lines in spectra which ware produced due water vapours. Spectrometer software measure absorbance, imaginary and real permitivity and transmittance etc. The conductivity which is produced due to imaginary permitivity [9-10] can be expressed as

$$\delta_{AC} = \omega\varepsilon'' \quad (3.14)$$

Where (ω) is the angular frequency measured in rad/s.

3.2.1.1: Reflectivity measurement by NRL arch method

NRL arch method was first introduced by united state naval research laboratory by measuring the reflectivity of plane materials over broad band. It consists of two horn atenna. One horn attenna was used for transmitting microwave signal and other was used for receiving the signals. Both of them ware connected with semicircle equipement at a fixed distance from the sample [11]. The transmitting antenna was attached with signal generator, while receiving attenna was connected with detector. Microwaves incident on the sample from transmitting antenna ware reflected back. Fig. 3.5 shows reflectivity measurement by NRL arches method, microwave are incident on sample backed by metallic plane at 5^0 with the help of source antenna, while reflecting waves are received by receiving antenna at 5^0.

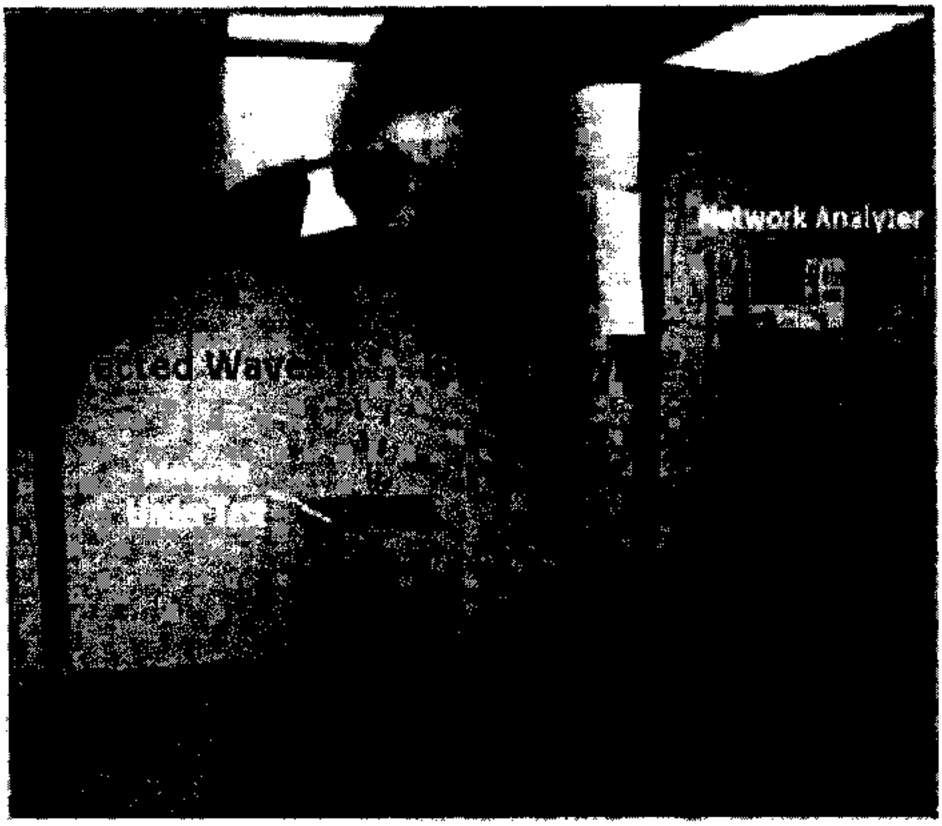

Fig. 3.5: *Reflectivity measurement by NRL arches method [12].*

Reflectivity is the logarithmic ratio of reflected signals P_2 to the incident signals P_1. So mathematically it can be expressed as

$$Reflectivity = 10\log_{10}\left({}^{P_2}/_{P_1}\right) \tag{3.15}$$

Similarly transmittance is the logarithmic ratio of transmitted signal P_3 to the incident signal P_1.

3.3: Scanning electron microscope (SEM)

SEM is the abbreviation of scanning electrons microscope. It was first introduced by Manford Von in 1937. It was developed due to limitation on light microscope. Scanning electron microscope uses electrons instead of light photon for the formation of image of specimen. It can produces more magnified image is compared to ordinary microscope due to shorter wavelength of electrons is compared to light photons [13]. Magnification of electron microscope is the ratio of length scanned at the surface of specimen to the scanned length of displaying screen.

So mathematically,

$$M = \frac{L_{scan\,specimen}}{L_{scan\,screen}} \tag{3.16}$$

Magnification of electron microscope can be increased by increasing the scanning length of specimen and decreasing the scanning length of screen.

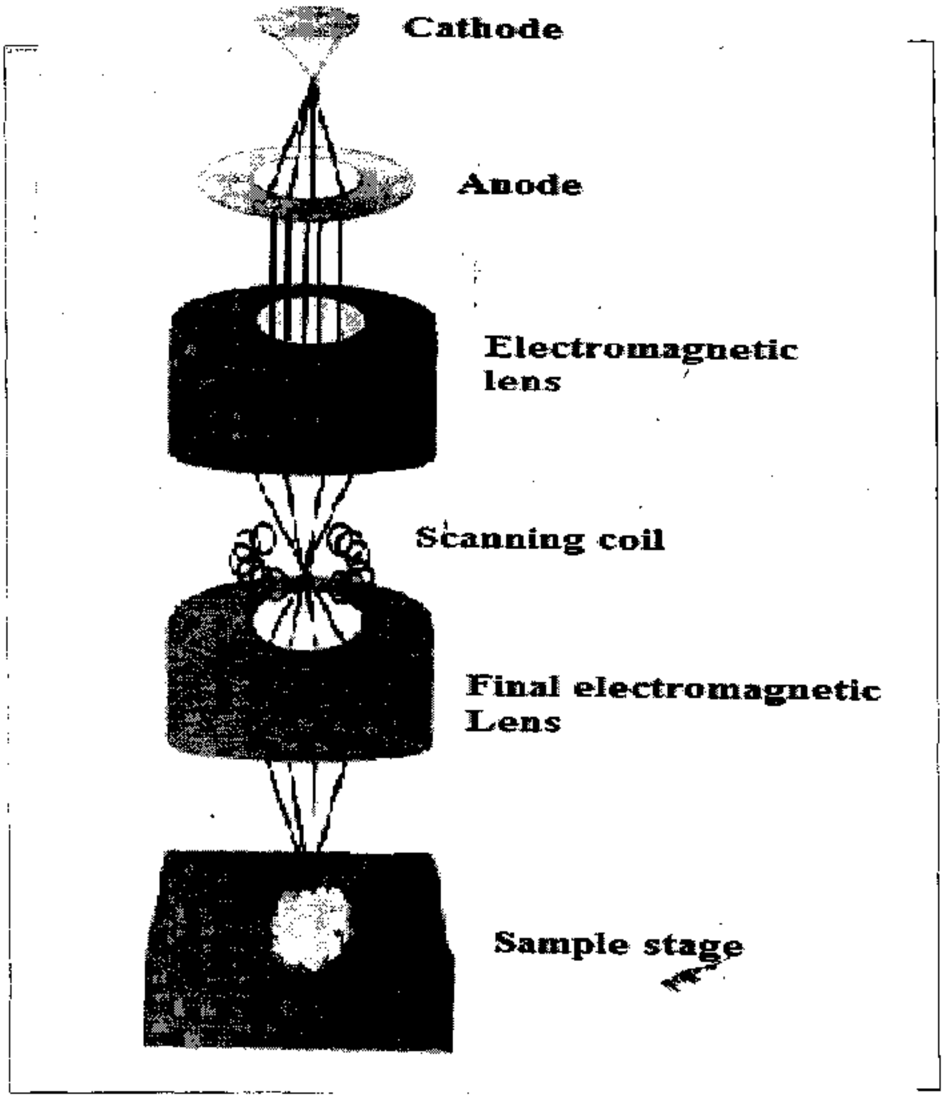

Fig. 3.6: Structure of scanning electron microscope [13].

Fig. 3.6 shows different parts of scanning electron microscope. Scanning electron microscope has the following parts.

- Electron gun
- Anode
- Electromagnetic lenses
- Scanning coil
- Secondary electron detector
- Backscattered electron detector
- TV screen

3.3.1: Electron gun

Electron gun is the basic source of producing a beam of electrons in scanning electron microscope. It consists of tungsten filament surrounded by Wehnelt electrode [14]. Tungsten filament produces a beam of electrons, when it is heated by applying potential deference across anode. This emitted electron passes through the small tip due to negative potential of Wehnelt electrode.

3.3.2: Anode

The anode is fixed below the electron gun. As anode is positive potential, so it will accelerate the beam of electrons in downward direction.

3.3.3: Electromagnetic lenses

Electromagnetic lens is made from a pair of copper wire enclosed in Iron pole pieces. When current is passed through the coil, magnetic field is produced in between the pole pieces of iron. This magnetic field will converge the beam of incident electron on the specimen placed it the stage.

3.3.4: Scanning coil

When incident beam of electrons collide with the specimen, it can produces weak beam of electromagnetic waves. Scanning coils are used to collect these electromagnetic waves.

3.3.5: Secondary electrons detector

When a beam of incident electrons collide with the surface of specimen, it will give energy to those electrons which are near to the surface [15]. Then those entire electrons which can gain sufficient energy will escape out from the surface of specimen. These escaped electrons are known as secondary electrons. These secondary electrons are collected by secondary electron detector of about 400 V. Further these secondary electrons ware accelerated toward phosphor screen by a potential difference of 2000 V. When secondary electrons collide with the phosphor screen, it will produce a flash of light. Photomultiplier converts flash of light into electrical signals, which can be viewed through video display and thus complete image of specimen can be viewed.

3.3.6: Backscattered electrons detector

When a beam of incident electrons collide with the atoms of specimen, they are scattered back. These scattered electrons are known as backscattered electrons [16]. Backscattered electrons are detected by a detector known as scintillator, which is fitted above the specimen. Backscattered give information about crystallographic structure of the specimen.

3.4: References

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Chapter: 4

Results and Discussion

Structure composites is made from both homogenous and composite materials. Their properties depend upon on constituent materials and composite structure design [1]. Structural composites are of two types.

- Laminar composites
- Honeycomb sandwich structure

4.1: Laminar composites

Laminar composites are made from five glass fiber layers (6/6 inch^2) coated with carbon nanofibers/epoxy composite solution by hand layup coated technique. First glass fiber was cut in desired shape of 6/6 inch^2. Then single glass fiber layers were coated by using a brush with composite solution. When composite solution completely wet the glass fiber layer, then second layer was placed on the coated layer. Similarly second layer was coated by a brush. So all the layers were coated one by one by the same procedure.

Afterwards, coated glass fiber sheets were placed in a glass mold. Peel ply was placed on the top face of coated glass fiber and breather on the top of peel ply. The whole structure was sealed with a vacuum beg. Vacuum pump was switched "on" to achieve the vacuum at room temperature at -1bar pressure. The coated glass fiber laminates were remained under vacuum for 4h. After 4h, the vacuum pump was switched "off", however glass fiber laminates were remained under vacuum to achieve solid laminar composite. Peel ply was removed from laminar composite and placed in an oven at 100^{0}C temperature for 4h for further curing. After curing, it will form a complete laminar composite.

4.2: Honeycomb sandwich structure

Sandwich structure was designed for lightweight structure panels having high stiffness and strength. A sandwich structure consists of two outer laminar composites bonded by a nomex honeycomb (5mm) by adhesive layers. Honeycomb layer will provide sharing stress to the sandwich panel and will elimsinate the multiple internal reflections of electromagnetic waves. In our present work, we have used CNFs/honeycomb sandwich structure for electromagnetic wave absorption in microwave region. Fig. 4.1(a) shows that five glass fiber layers were coated by hand layup method and then coated layers were placed under vacuum which form solid thin nanocomposites.

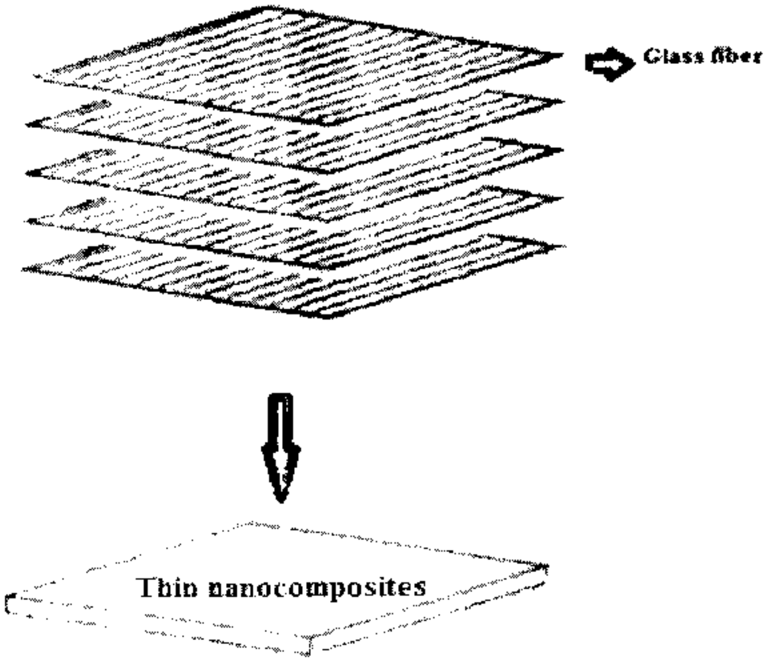

Fig. 4.1 (a): Structure of laminar composites [1].

Fig. 4.1(b) shows the structure of honeycomb sandwich structure. 5 mm honeycomb were placed in between CNFs absorbing sheets with the help of adhesive layers by using hydralic press.

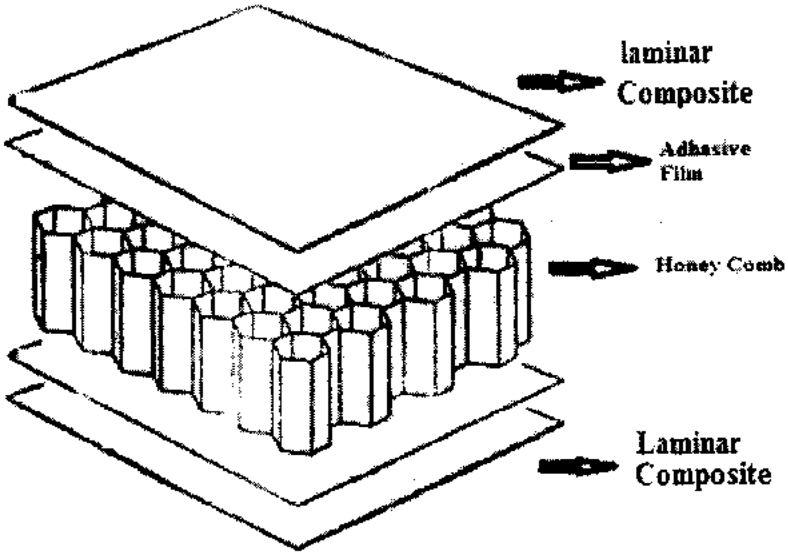

Fig. 4.1 (b): CNFs / honeycomb sandwich structure [1].

4.3: SEM images of carbon nanofibers absorbing sheets

Fig. 4.2 (a) and Fig. 4.2 (b) shows the SEM images of carbon nanofiber absorbing sheets. Epoxy resin can be seen in between glass fiber, when image was taken at a magnification of 20,000-50,000 but carbon nanofibers were not observable in these images.

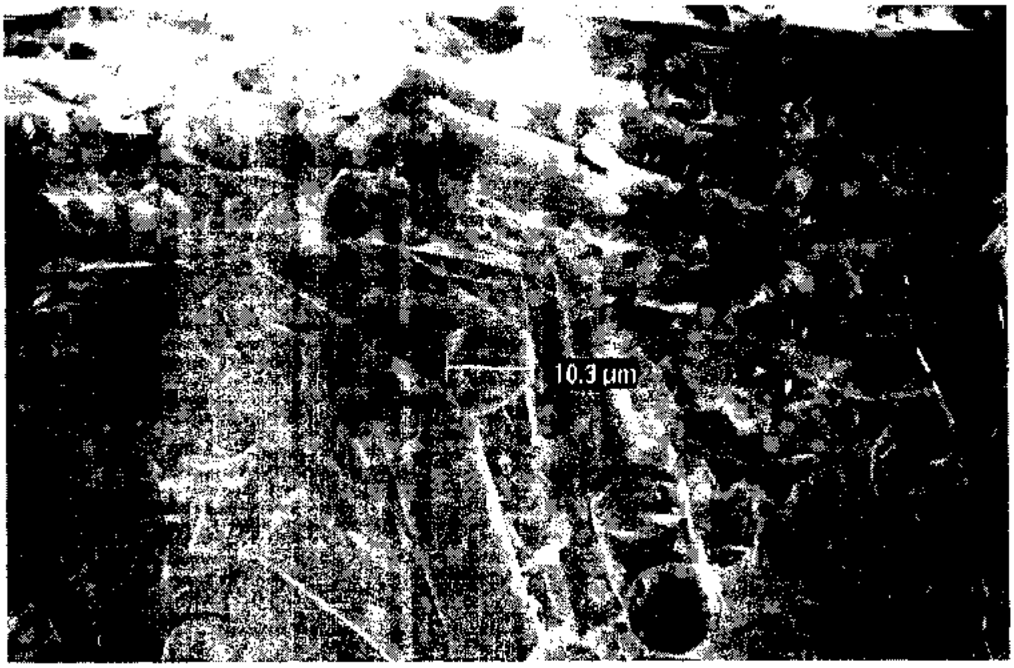

Fig. 4.2 (a): Glass fiber along with epoxy resin inside carbon nanofibers 2wt% absorbing sheet.

Fig. 4.2 (b): Epoxy resin inside glass fiber in carbon nanofibers 4wt% absorbing sheet.

4.4: Introduction

The properties of nanocomposites microwave absorbers depend on the electrical conductivity, which is the function of wt% of nanofiller in the epoxy matrix. In dielectric type microwave absorbers, the parameter which ultimately determine the strength of the absorber is the complex permittivity ($\varepsilon = \acute{\varepsilon} - j\,\varepsilon''$) [2]. Where $\acute{\varepsilon}$ and ε'' are the dielectric constant and dielectric loss factor, respectively. The imaginary part ε'' of permittivity which is responsible for the absorption of microwaves is directly proportional to the electrical conductivity of the absorber as given below

$$\delta_{Ac} = 2\pi\varepsilon_0\varepsilon''\mathrm{f}$$

OR

$$\varepsilon'' = \delta_{Ac}/2\varepsilon_0\pi f \qquad (4.1)$$

Where ε_0 is the permittivity of free space. According to Eq. (4.1) one could infer that higher δ_{Ac}, higher will be the dielectric loss factor ε''. But the case is not so simple, because ⍰$_{Ac}$ can be increase to a certain limit beyond which the material becomes a perfect reflector of microwaves instead of absorbing them. The tangent loss given in Eq. (4.2) determines the strength of a microwaves absorber,

$$\tan loss\ (\tan\delta) = \varepsilon''/\acute{\varepsilon} \qquad (4.2)$$

- Higher the tan⍰, higher will be the absorption, however, ε'' should be such that to avoid the reflection.

In the present work we have used carbon nanofibers, as filling material in the glass fiber/epoxy composite to make a microwave absorber. The concentration of the nanofiller was varied to get the optimum CNFs filler wt%. The result and dissection section has been divided into two sections. In section I, thin nanocomposites sheet were prepared by varying the CNFs wt% (2,3,4 and 5) and these sheets were used to make sandwich structure (nanocomposites/honeycomb core/carbon fiber). Section II, the microwave absorption properties of hybrid composites in which CNTs and graphene nanoplatelts have been used as filler along with CNFs are discussed.

4.5: Thin nanocomposites:

The result of complex permittivity measurement for E-glass/epoxy composites filled with carbon nanofiber in 2, 3, 4 and 5 wt% in Ku band (11-17 GHz) of microwaves are shown in Figs. 4.3 and 4.4. In can be seen from Fig. 4.3 that dielectric constant (έ) has been increased from 4.8 to 6.7 at 11 GHz with CNFs filling upto 4 wt%, which has been decreased to 6.2 with further increase of the concentration of nanofiber to 5wt% [3]. However, the variation of dielectric constant as a function of frequency for all samples is similar, which is typical for dielectric materials. The dielectric constant has been decreased with the increase of frequency in all samples. The real part of permittivity (dielectric constant) represents the degree of polarization in response to the applied field. With the increase of the frequency of the electromagnetic field the atoms, molecules and electrons etc are not able to follow the rapid changes in the applied electromagnetic field that is why dielectric constant is decreased. The possible reason of the decrease in the dielectric constant for 5wt% CNFs is the poor dispersion of the nanofiber in epoxy matrix.

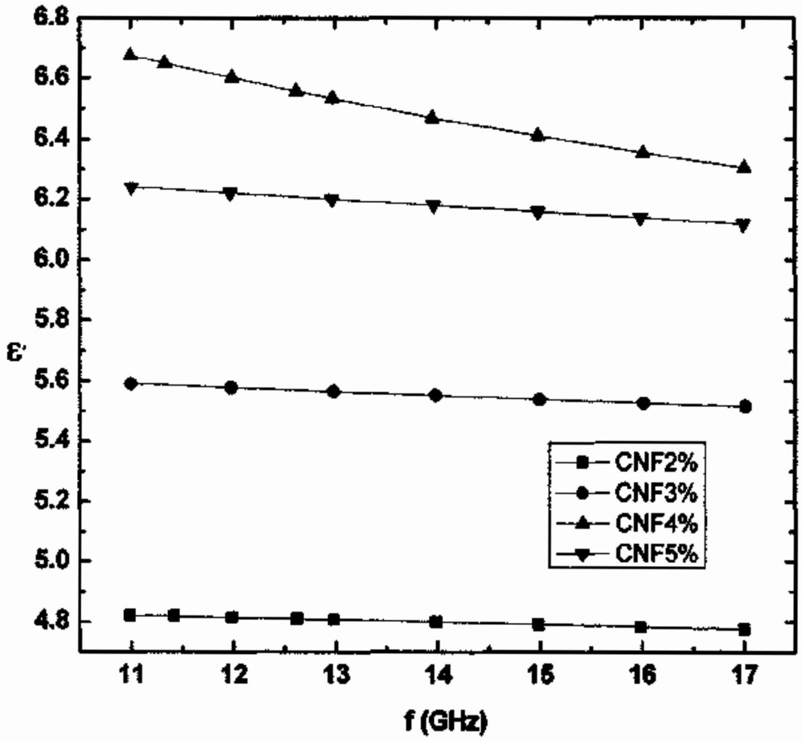

Fig. 4.3: *Real permittivity of CNFs absorbing sheets in Ku frequency band.*

In Fig. 4.4 shows the imaginary part (έ) of the complex permittivity of composites in the Ku frequency band. The dielectric loss factor (ε") has shown similar behavior as έ. The magnitude of ε" depends upon the eddy current losses and the fractional forces of the material, which resist the polarization of the atomic species. The eddy current losses depend on the conductivity network formed by the CNFs in the epoxy matrix. If the dispersion of the nanofiller is very good, there should be a sharp increase in the electrical conductivity at a certain wt % of CNFs. The decrease in ε" at 5 wt% might be due to poor CNFs dispersion due to higher concentration of CNFs which are unable to make a conductive network. The nanofibers have higher surface area, which provide higher interface with the epoxy matrix. Such large interface area provide interface polarization resulting in higher ε", but at higher concentration the chances of agglomeration of CNFs is higher, which ultimately reduces available surface area and hence ε".

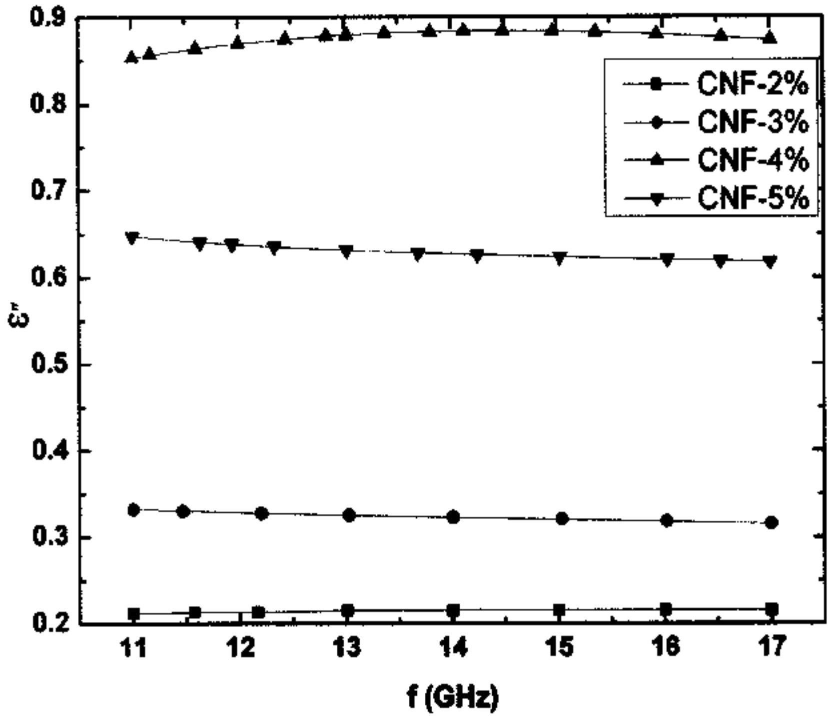

Fig. 4.4: *Dielectric losses of CNFs absorbing sheets in Ku frequency band.*

The tangent loss which represents the losses in the material is shown in Fig. 4.5 for all concentration of CNFs. It can be seen from Fig. 4.5 that tangent loss increases with the increase of nanofiller upto 4wt%, which has been decreased at 5wt% of carbon nanofibers. The magnitude of tan loss shows the expected loss of microwave energy in the nanocomposite would be very small. It has been observed that the microwave absorption with higher reflection loss possess higher value of tin loss.

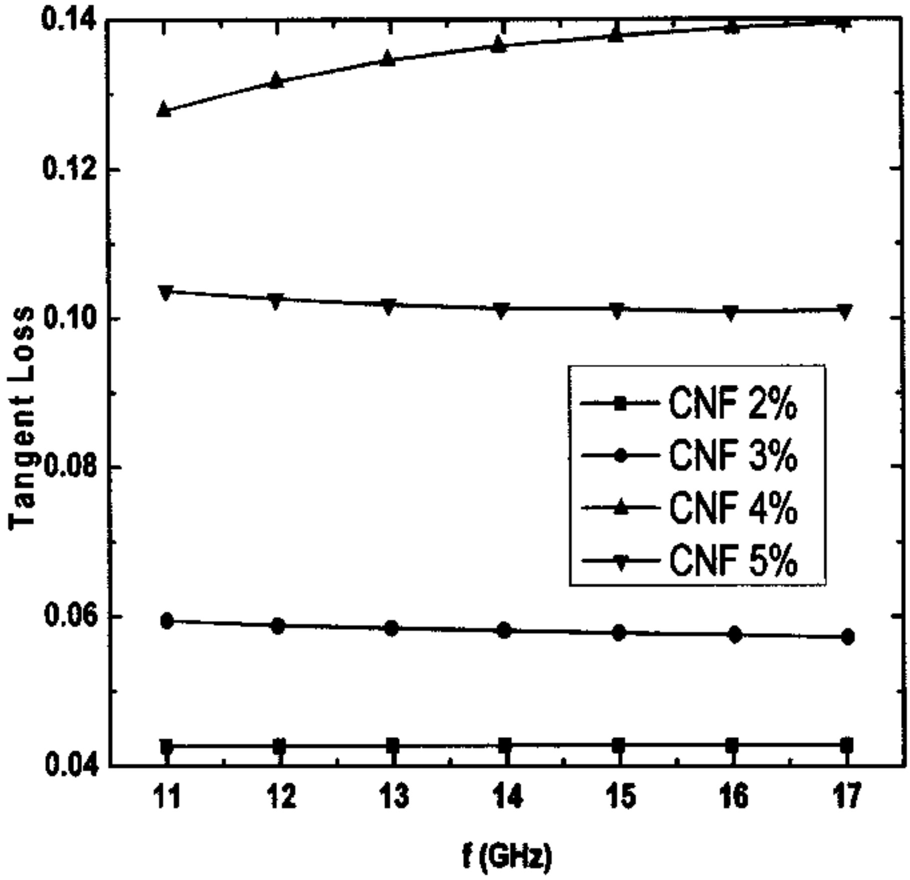

Fig. 4.5: *Tangent loss of CNFs absorbing sheets in Ku frequency band.*

The scattering parameters [4] S_{21}, which represents the transmission loss from the microwaves absorber, respectively. The scattering parameter S_{21} were found by using free space method [5] as shown in Fig. 4.6 for all concentration of nanofiller.

The S_{21} parameter [6] which is associated with transmission loss is also increased with the increase of nanofiller concentration. The shape of the S_{21} curves is possibly due to the depth dependent loss of microwaves due to the concentration gradient through the thickness of the samples.

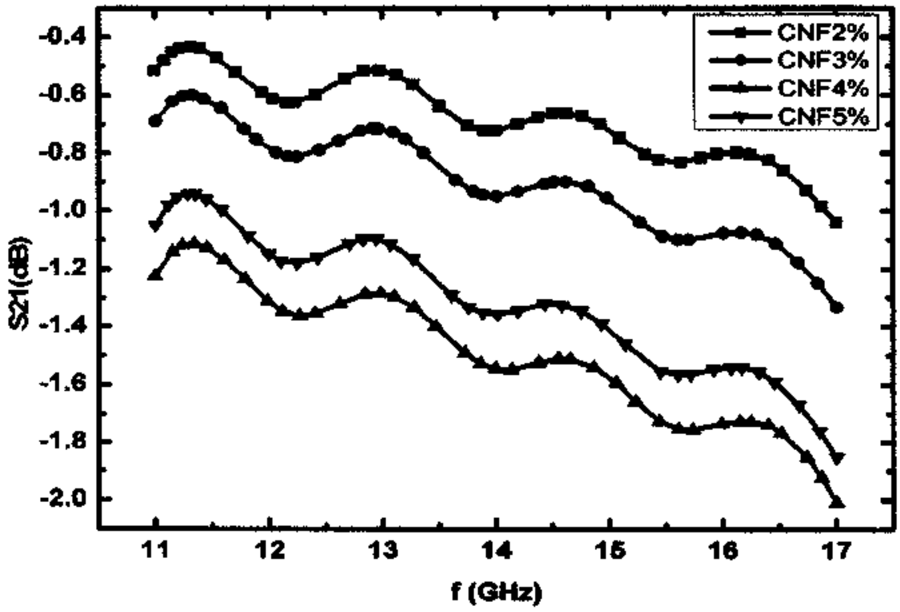

Fig. 4.6: *Transmation loss of CNFs absorbing sheets in Ku frequency band.*

The reflection of microwaves can be also be minimized by using a quarter wavelength absorbers. According to Eq. (4.3), if the thickness of the absorbers is quarter wavelength, then the incident and reflected wave will be out of phase by 180^0, which can cancel the effect of each other due to destructive interference.

$$t = \lambda_0 \,/4\sqrt{\acute{\varepsilon}} \qquad (4.3)$$

Where λ_0 is the resonant wavelength and $\acute{\varepsilon}$ is the real part of permittivity. The schematic of a quarter wavelength absorber is shown in Fig. 4.7.

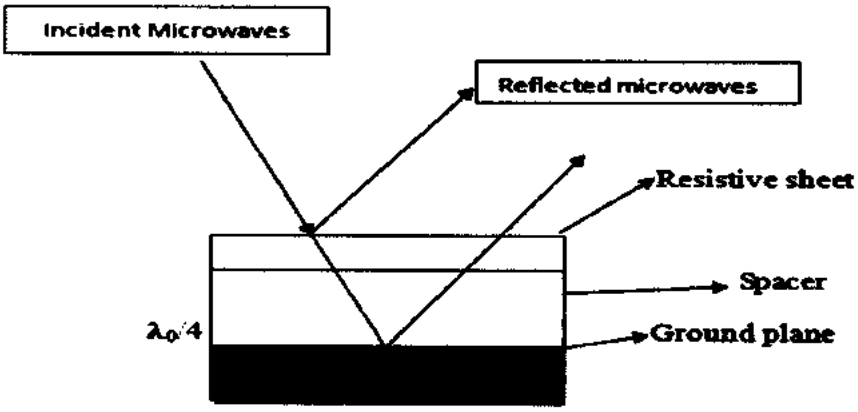

Fig. 4.7: Reflection from microwave absorber.

The resonant absorber consists of a thin resistive sheet at a quarter wavelength separation from between the nanocomposites sheet and the ground plane .It can be seen from this Fig. 4.8, that the reflection loss has been decreased after using spacer, which shows that the thickness of the spacer is not following the quarter wavelength condition. Due to this instead of cancelation of the incoming wave both reflected and transmitted waves are reinforcing each other, resulting in the enhancement of the signal of the reflected wave.

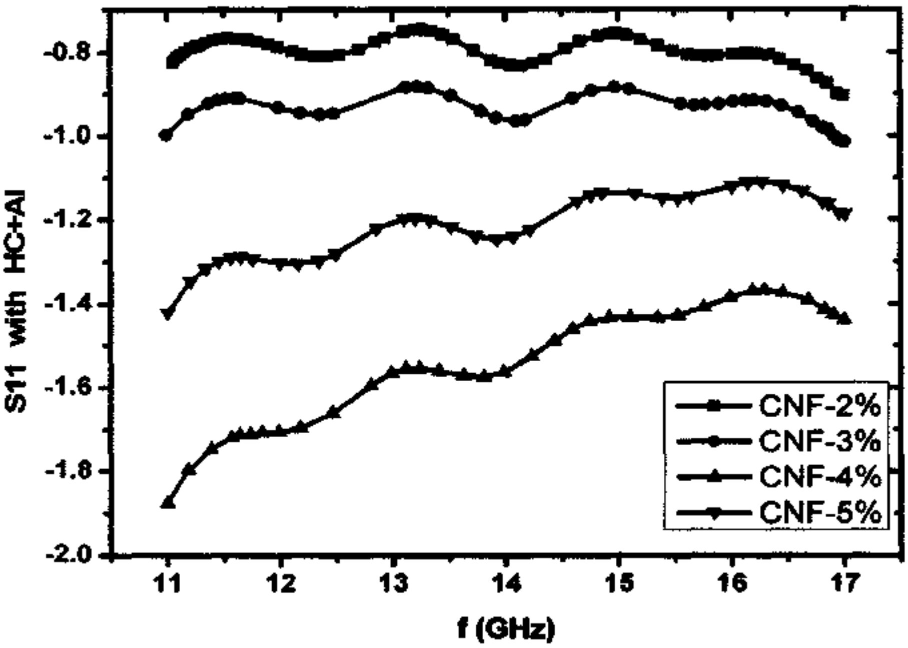

Fig. 4.8: Reflection loss of CNFs absorbing sheets in Ku frequency band.

4.6: Hybrid nanocomposite

Hybrid nanocomposites are made from the combinations of two or more than two nanomaterial have particle size less than 100 nm. We have made four different types of hybrid nanocomposite. i.e. Carbon nanotubes hybrid nanocomposites and graphene hybrid composites. Carbon nanotubes hybrid nanocomposites (CNF-C) ware formed by mixing carbon nano fiber of 1.5 wt% with carbon nanotubes of 0.5 wt%. Similar graphene hybrid nanocomposites (CNF-G) were formed by mixing 2 wt% of carbon nanofiber with 0.5 wt% of graphene. It has been observed from previous section that even at higher concentration of carbon nanofibers upto 5wt% the dielectric factor (ε") or tangent loss are not so much significant to induce microwaves absorption properties in glass fiber/epoxy nanocomposites. Therefore in order to optimize dielectric properties of

Fig. 4.9: Reflection loss as a function of frequency.

nanocomposites, hybrid composite filled with two types of nanofiller i.e. Carbon nanofibers, carbon nanotubes and graphene nanocomposites have been prepared. Initially, the electrical conductivity of nanocomposites was measured to select best filler wt%.

The dc electrical conductivity [8] of nanocomposites as a function of filler concentration of CNF is shown in Fig. 4.9. It can be seen from this Fig. 4.10 that conductivity increases [7] upto 2wt%, which is three times higher than that of 0.5wt% concentration. The sharp increase in conductivity is due to the formation of conducting network formed by carbon nanofibers. The dc conductivity start decreasing upon further increase of CNF wt%. The reason is the increase of viscosity of the matrix and the agglomeration of nanofiller at such higher concentration, suppressing the conductivity network formation.

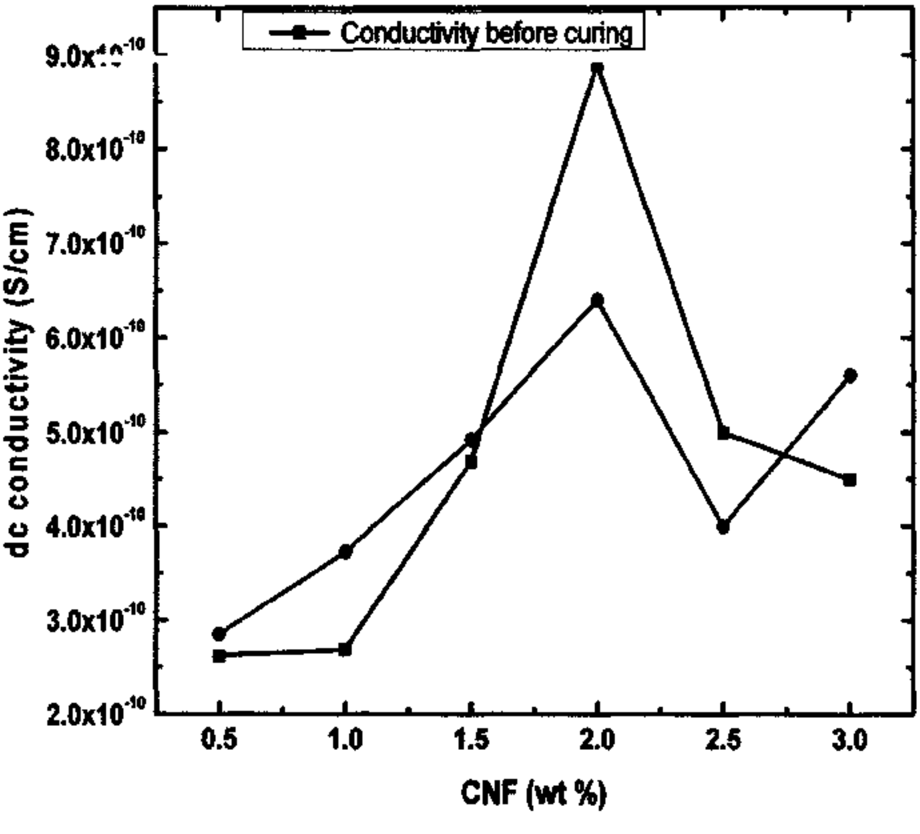

Fig. 4.9: Conductivity of CNFs samples w.r.t CNF weight

Following the result of electrical conductivity as shown in Fig. 4.9, two best concentration of CNFs wt% have been used to make composite samples to determine the strength of microwave absorption. The results are shown in Fig. 4.10 in frequency range 2-18 GHz. It can be seen from Fig.

4.10 that reflection loss is higher for 2wt% concentration, which is -2.5dB at 18 GHz, however this concentration is not sufficient for practical purpose. Fig. 4.10 shows the comparison of front side of carbon nanofiber absorbing sheets with two types of hybrid nanocomposites from front side. CNF 1%-F and CNF 2%-F represents front side of carbon nanofiber absorbing sheets. Similarly CNFC-F represents front side of carbon nanotubes hybrid nanocomposites and CNFG-F represents front side of graphene hybrid composite.

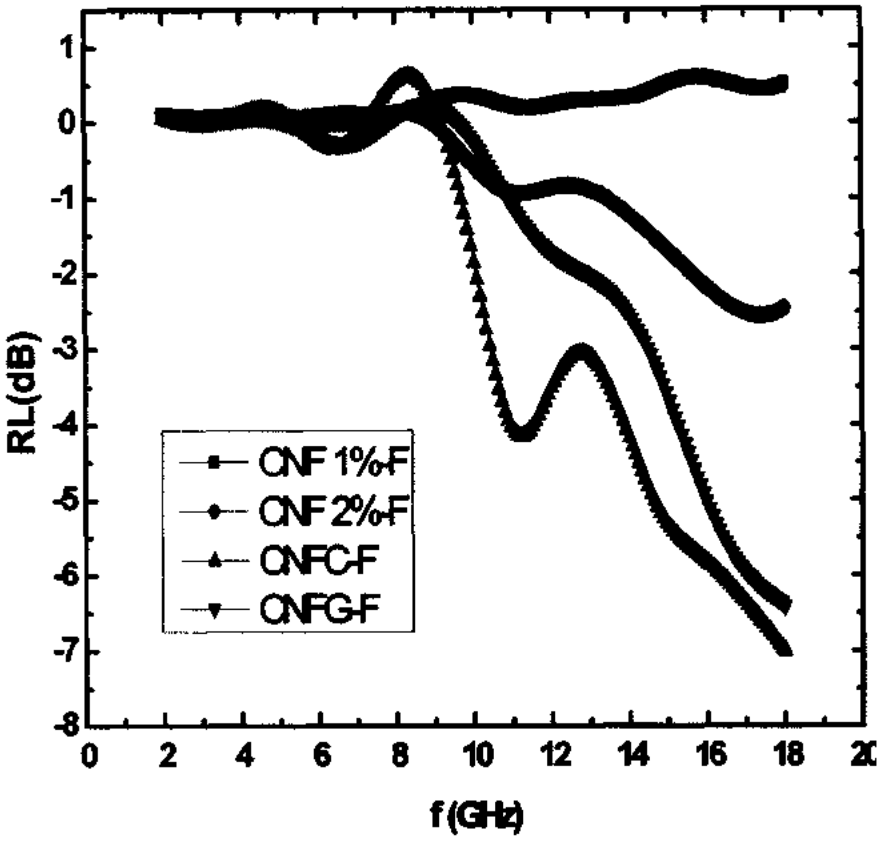

Fig. 4.10: Reflection loss of hybrid nanocomposites as a function of frequency from front side.

Fig. 4.11 shows the comparison of carbon nanofiber composites with hybrid nanocomposites from back side. CNFC-B represent back side of carbon nanotubes hybrid nanocomposites and CNFG-B represents back side of graphene hybrid composites. Similar CNF 1%-B represents back side of 1wt% of carbon nanofiber nanocomposite and CNF 2%-B represents back side of 2 wt% of carbon nanofiber nanocomposite.

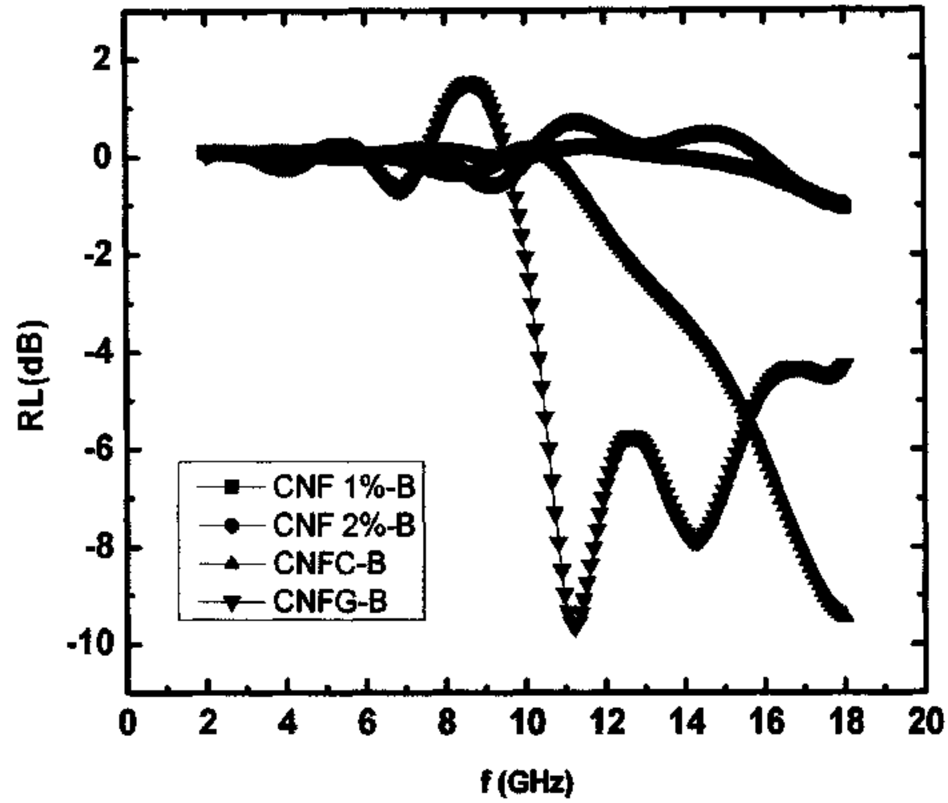

Fig. 4.11: *Reflection loss of hybrid nanocomposites as a function of frequency from back side.*

Carbon nanotubes tubes are known to have very high electrical conductivity and aspect ratio which make them very potential nano materials for electrical properties. Therefore in order to enhance [9] the electrical conductivity of the composites 0.5wt% of carbon nano tubes (CNTs) have been used and the concentration of carbon nanofibers was varied.

The electrical conductivity [10] of hybrid composite as a function of carbon nano fiber concentration for fixed wt% carbon nano tubes [7] is shown in Fig. 4.12. It can be seen from this Fig. 4.12 that electrical conductivity has been increased [11] by two orders of magnitude by the addition of MWCNTs. Moreover highest conductivity is achieved at 1.5wt%

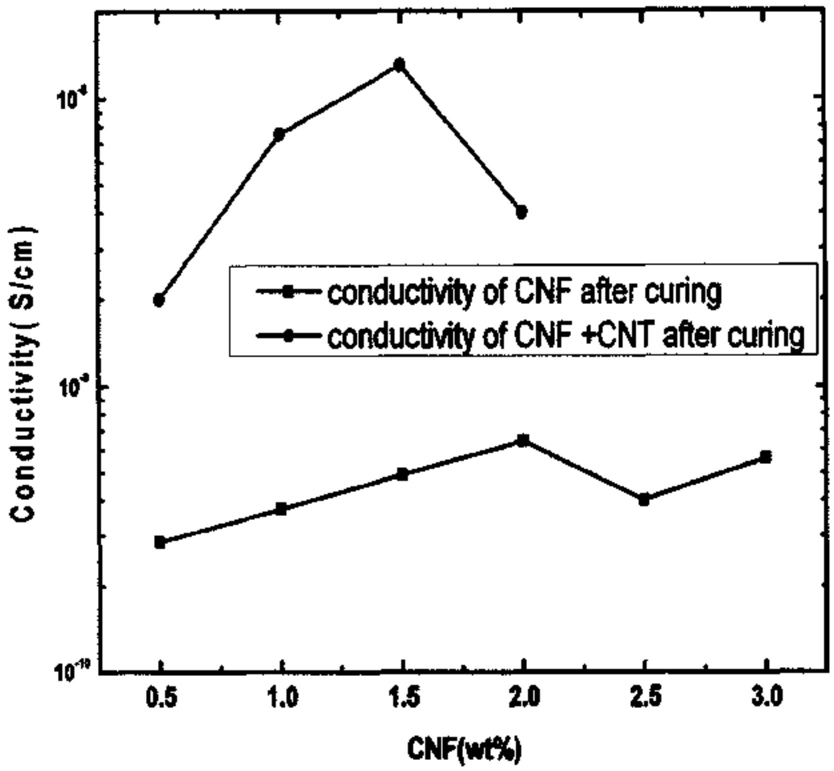

Fig. 4.12: *Conductivity as a function of weight fraction of CNFs.*

Fig. 4.13 shows conductivity of carbon nanofiber at different sonication time. Conductivity depends on well separation, well distribution and composites percolation threshold of CNFs particles. Conductivity at 45 minutes Sonication shows two orders higher conductivity at 45 minutes sonication than 15 and 30 minutes sonication [12]. This increase in conductivity is due to well dispersion, well distribution and well conductive network form between the carbon nanofiber particles. The conductivity at 15 minutes sonication is due to will dispersion but bed distribution of CNFs particles. At 30 minutes sanction, there is bed separation and bed distribution as a result conductivity decreases [13]. At 60 minutes sonication, there is well separation and well distribution between CNFs particles but a weak percolation threshold due to breaking of CNTs which results in decrease of conductivity [14-15].

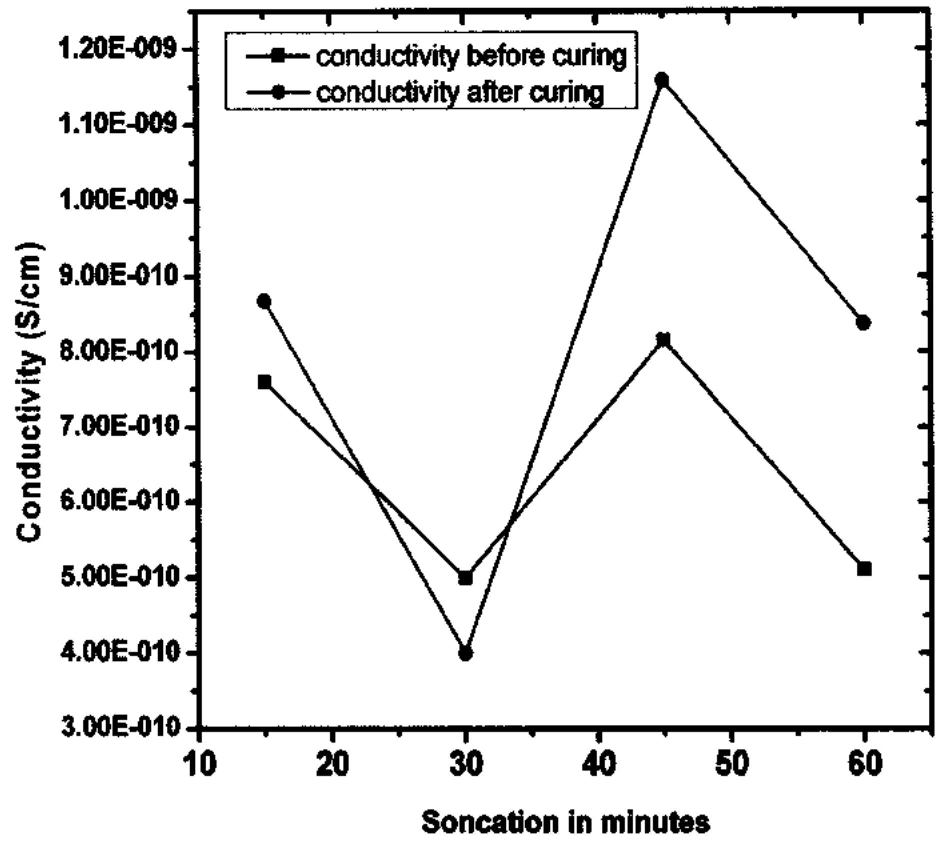

Fig. 4.13: *Conductivity of CNFs samples w.r.t sonication time.*

4.7: Conclusion

In the present work we have prepared nanocomposite sheets (CNF-2, CNF-3, CNF-4 and CNF-5) by vacuum bagging technique for microwave absorption at different CNFs weight fraction

(2wt%,3wt%,4wt% and 5wt%) in epoxy/glass fiber composites. The strength of these microwave absorber depends on the complex permittivity. Real and imaginary permittivity increases with increase of nano filler concentration upto 4wt% due increase in atomic polarization and eddy current losses but decrease at 5wt% due to poor dispersion of Carbon nanofibers in epoxy resin.

Similar behavior was observed in and transmission losses with nanofiller concentration upto 4wt%, than deceases at 5wt% concentration . Also transmission losses increase with increase of filler concentration at higher frequency due to depth dependence of microwave absorption in absorber.

To decrease the reflection losses of microwave absorber, quarter wavelength absorber was prepared. Thin resistive sheet was placed at quarter wavelength from ground plane by placing Nomex honey comb (5mm) as a spacer from ground plane. Reflection losses were small, but its thickness does not obey quarter wave length condition due to which reflection and transmission enhances. The maximum reflection loss for carbon nanofiber absorbing sheets at 18 GHz was -2.5 dB .

To enhance the reflection losses in microwave absorbers, hybrid nanocomposites were prepared by filling (0.5 wt%) of carbon nanotubes and graphene in 2wt% of carbon nanofibers composites. Due to hybrid nanocomposites, reflection loss decreases from -2.5 dB to -9.7 dB. So in future hybrid nanocomposites of graphene and carbon nanotubes along with carbon nanofiber composites can be prepared for better electromagnetic shielding.

4.8: References

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