ENVIRONMENTAL STUDY OF NANO-FILLER EMBEDDED FIBER REINFORCED POLYMER COMPOSITE

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CERTIFICATE

This is to certify that the thesis entitled, **'Environmental Study of Nano-Filler Embedded Fiber Reinforced Polymer Composite'** submitted by **Hem Shruti Bhardwaj (111MM0357)** and **Prangya Paramita Sahoo (111MM0378)** in partial fulfilment of the requirements for the Degree of Bachelor of Technology in Metallurgical & Materials Engineering at the National Institute Of Technology, Rourkela is a bonafide and authentic research work carried out by them under my supervision and guidance for over the last one year (2014-15).

To the best of my knowledge, the work embodied in this thesis has not been submitted earlier, in part or full, to any other university or institution for the award of any Degree or Diploma.

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CONTENTS

ABSTRACT

Fiber reinforced polymer (FRP) composites have a huge demand for applications in diversified fields because of their unique combination of properties. Inspite of having many advantages, these composites are susceptible to degradation when exposed to harsh environmental conditions which limits their use. CNTs have proved to be an ideal and most suitable reinforcing element to manufacture advanced materials such as nanocomposites. GFRP composites were fabricated with 0.1wt%, 0.3wt%, and 0.5wt% CNT. Introducing a low wt.% CNT up to 0.3% showed significant increase in mechanical properties such as flexural strength, ILSS, Storage modulus of GFRP due to better fiber/matrix interfacial bonding whereas a higher wt.% CNT showed not much improvement due to agglomeration of CNTs in the matrix. During the fabrication, period of service and storage of components made up of these polymer materials, they are operating under changing environments which affects the predictability and reliability of the long term as well as the short term properties and also their in-service performance. This work is also an attempt to highlight the degradations that may be caused to the GFRP as well as CNT reinforced GFRP composites on exposing to various environmental conditions such as UV radiation, 95% Relative Humidity at $60^{o}C$ and Hot Water at $60^{o}C$. Short beam shear test as well as Dynamic Mechanical Analysis of conditioned samples in all the three cases showed a significant decrease in mechanical properties of the composite systems. There was also a very slight increase in the glass transition temperature due to these exposures. DMA study was conducted on all the composite systems with an isothermal holding at $90^{o}C$ and $110^{o}C$ with different holding time periods and their behaviour were analysed. Incorporation of a low wt.% CNT reinforcement is found to lessen the degradation effect of the exposure environment on the polymer matrix and 0.3wt.% CNT-GE composite demonstrated an overall better performance under all kinds of exposure.

KEYWORDS: CNT reinforced GFRP, UV radiation, Relative Humidity, Isothermal Holding, Short Beam Shear test, DMA, ILSS.

CHAPTER 1

INTRODUCTION

1.1   Composites

A judicious combination of two or more elements, which exhibit their own distinct identities, to form a material having a unique combination of exceptionally improved properties is known as a composite material. The idea of composite materials has provided the freedom to engineer properties according to the desired needs. It generally consists of two basic components- the continuous phase called the matrix phase and the reinforcement, which is the dispersed strengthening phase of the composite. The all-round properties of composites depend on the individual properties of its constituent materials, the geometry of the reinforcing phase and their relative proportions in the composite.

Fibre-reinforced polymer is a type of composite material in which the polymer matrix is reinforced with fibers. The fibres employed are usually glass fibres, carbon fibres, or aramid fibres. The polymer is mostly epoxy resin, vinylester or polyester, PMMA, HDPE, and phenolic resins.
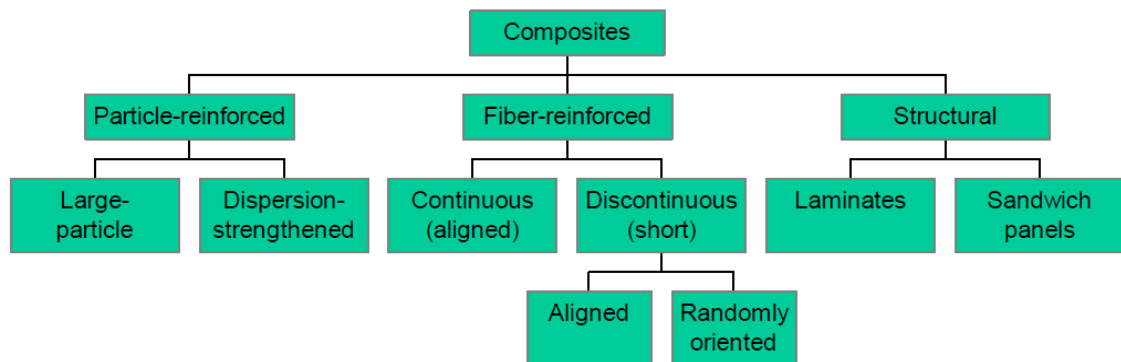
Figure 1.1: Classification of Composites

1.2   Matrix

The continuous phase of the composite that holds together the reinforcement materials and maintains the integrity of the composite by transferring load to the reinforcing phase is known as matrix. It also protects the reinforcements dispersed in it from damage due to various external factors. Mostly used matrix materials are of three types- metals, polymers and ceramics.

1.2.1 Polymer Matrix

An organic material which is composed of molecules made from repetitions of the same monomers is known as a polymer. They have a lower modulus and strength, low temperature tolerance and is susceptible to degradation by moisture. They are of two types: thermosets and thermoplastics.

1.2.1.1 Thermosets and Thermoplastics

Thermosetting polymers are generally made from liquid or semisolid precursors which undergo irreversible hardening by polymerization or curing and at the end the resin (liquid) is converted to a very hard solid by the process of cross linking which results in 3D networks of polymer chains. The common polymers employed are the epoxies, vinyl ester, polyester and phenolic resin.

Thermoplastics are polymers which show softening and melt on heating. They have an amorphous structure and randomly arranged polymeric chain and are suited for processes of forming by easy flow of liquid on heating. Some common thermoplastics are PMMA, high density polystyrene, low density polystyrene and polyethylene.

1.2.1.2 Epoxy Resin

It is the most widely used matrix material (polymer) which is available ranging from low viscous liquids to solids of high melting point and can be modified to a wide range for use. They offer a low shrinkage, high strength, easy and rapid curing by different of curing agents, better electric insulation, proper bonding and wettability. These properties make them ideally suited for use in composites. In epoxies, cross-linking takes place of groups of epoxide (between two carbon atoms and an oxygen atom). The most generally used epoxy is diglycidyl ether of bisphenol A (DGEBA).

1.3   Reinforcement

Reinforcements used in the composites can be fibers, whiskers or particles. Fibers may be continuous of discontinuous (short). Particles bear no preferable orientation and neither any shape. High strength whiskers have a preferable shape but are monocrystalline and very small

both in length as well as in diameter with respect to fibers. Reinforcements in composites provide the strength to the composite, heat resistance, corrosion strength and rigidity.

1.3.1   Glass Fibres

Glass fibers are made of glass compounds based on silica that contain various metal oxides which can be engineered to create a variety of glass. Apart from the main oxide content which is silica, Na, Ca and Al oxides are also introduced to decrease melting point and disrupt crystallization. The three common types of glass fibres are:

- E-glass: E glass fiber has a very less content of alkali in it. It is used for applications in building structures and in construction industries, it has good resistance to heat and electricity.
- S-glass: It contains magnesium alumina silicate used where high strength, high stiffness, extreme temperature resistance is needed.
- C-glass: It is a calcium borosilicate glass which is corrosive resistant and is used in acid corrosive environments.

1.3.2   Nano-fillers

Introduction of these second phase inclusion particles (fillers) which result in toughening through mechanisms such as deflection and pinning of cracks, micro-cracking, rubber cavitation, shear banding and bridging (hard filler) or particle tearing (soft fillers). However, incorporation of soft particles has disadvantages such as lowering of glass transition temperature (Tg), modulus and strength of laminate of composites. Nanoparticles results in decrease in initiation of microcracks and can greatly improve the tolerance of laminated composites. The factors affecting these mechanisms include volume fraction of fillers, bonding at the interface, size and shape of the nanofillers. In case of nanosilica fillers improvement in fracture toughness is because of the debonding effect of the filler and subsequent growth of plastic voids.

CNTs possess unique mechanical properties which includes high stiffness, strength and resilience. The Young's modulus of CNTs is more than 1.0 TPa, and the tensile strength is in between 200 and 500 GPa. As a result, CNTs are utilized for the development of new material systems, particularly, structural nanocomposites. On adding carbon nanotubes in composites, the mechanism of bridging restricts the growth and propagation of crack and

improves the toughness of the material. Moreover, during fiber pull-out high increase in fracture energy can be due to the enhanced interface area. Moreover, the weaker strength van der Waals forces at the interfaces could cause slippage at the interface which can thereby result in inefficient transfer of load to fibres via the matrix and prevent attainment of high strength in composites. Addition of very low amount of fillers of the size of nanometres significantly increases matrix properties by effectively transferring load at the interface. CNT also has a plasticization effect on polymers by increasing its free volume and hence lowering the glass transition temperature. Plasticization effect is increased by the presence of voids in the material system.

1.4   Interface

A 3D region between the fibre and the matrix is known as the interphase. It is not just the 2D area of bonding between the fibre and the matrix, but also has some definite thickness on both the sides of the fiber-matrix interface, wherein the chemical, mechanical and physical properties show a sudden change between the fiber and the matrix. The efficiency of composites depends not only on the constituent fiber and matrix properties but also on nature of the interface between them. Transmission of the load from the matrix to the fibers takes place at the interface, which contribute the larger portion of the composite strength. More the interfacial bonding better will be the Inter Laminar Shear Strength, de-lamination resistance, fatigue and corrosion resistance. Addition of nanoparticles increases the interfacial area and hence improves the interfacial bonding and load transfer between matrix and fibres.
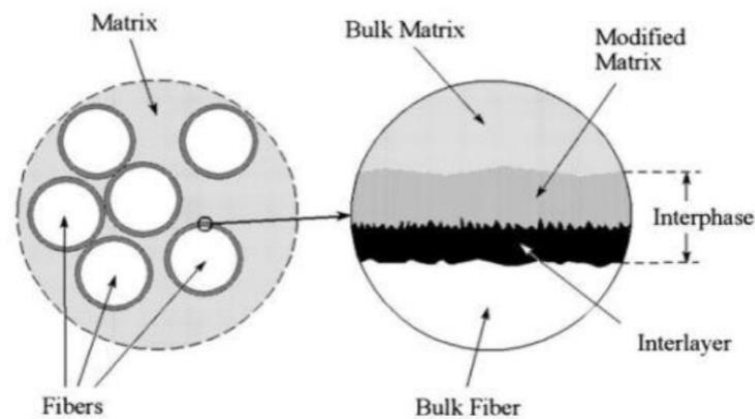
Figure 1.2: Schematic representation of a composite interphase

1.5   Applications of FRP composites

Increased number of engineering and structural applications requiring high performance has made FRP composite materials very important in the present scenario. FRP materials have many alluring mechanical properties for manufacturers and designers. The outstanding mechanical properties such as better damping characteristics, high strength to weight ratio, resistance to corrosion, good impact strength, and high fatigue strength enables their use in many diverse applications. Extensive applications of FRPs include its usage in various structures and components of aircrafts, automobiles, aeroplanes, space vehicles, boat hulls, ships, chemical equipment and vessels, pipelines, sports equipment, and infrastructures such as buildings and various kinds of bridges.

Figure 1.3: Applications of FRP materials in diverse fields

1.6   Limitations of FRP composites

All the above components and structures made of FRP materials are exposed to some environmental conditions during their service. These environmental conditions can be high temperatures and low temperatures, high relative humidity, alkaline environment, UV

radiation exposure and can be more critical if there is a cyclic continuous variation of temperature, thermal spike, low earth orbit space environment and hygrothermal exposure.

Fiber reinforced polymer composites are more sensitive to damage in these environmental conditions. The mechanical behaviour of FRP composites are more influenced by the interfacial bonding at the fiber-matrix interface. High difference in coefficient of thermal expansion of fiber and matrix can lead to differential expansion at elevated temperature and can degrade the interfacial bonding which causes lowering of ILSS of the composite. On the other hand, at low temperature the polymer matrix behaves in a brittle manner and prevents the removal of internal residual stresses or accumulation of stresses. The internal residual stresses at extremely low temperature may results in large debonding at the interfaces. The moisture present at the interface can alter the interfacial bonding by chemical reactions at the interface thus affecting the mechanical properties of the FRP composites. Despite of having many positive aspects of utilizing FRP's, they are susceptible to maintain their excellent performance against the severe environmental conditions.

CHAPTER 2

LITERATURE REVIEW

2.1   Effect of Ultra Violet radiation on FRP composites

Polymeric materials are very susceptible to UV radiation [1]. The energy of the UV radiation is capable of dissociating the molecular bonds of chains in polymer matrix and may lead to the degradation of many properties of the composite materials [2]. These degradations include the breakage of various chemical bonds, forming free radicals which result in permanent chain scission or in cross-linking, depending on the kind of polymer in consideration, the wavelength of the UV radiation used and other factors [3]. Chemical reactions induced due to UV exposure are the result of a complex set of reactions involving the synergistic effect of UV and oxygen [4]. The main mechanism of photo-initiated degradation is the similar for all polymer materials according to which damage takes place when photons react with the chain molecules of the polymer structures [5].

UV spectrum can be divided into three types depending on the wavelength: UV-A portion of the spectrum (400–315 nm) is very less damaging to organic polymers and forms around 6% of the total radiation of sun which reaches the earth; UV-B (315–280 nm) which is a more damaging type and forms about 0.1% of total radiation; and UV-C (280 nm) which is the most degrading of all to the polymers [6]. However, UV-C is screened out by the atmosphere of atmosphere. Polymeric materials greatly absorb the short wavelength having higher energy of photons which have the capability to break chemical bonds in that material [7].

There is no uniformity of degradation caused by UV light in the polymer, but specifically in case of opaque materials, the damaging effects are observed more on or near the surface. The two most commonly observed effects are loss of gloss and change in colour [8]. It also leads to a reduction in molecular weight and hence a loss in elastic nature, cracking and reduction in the mechanical properties.
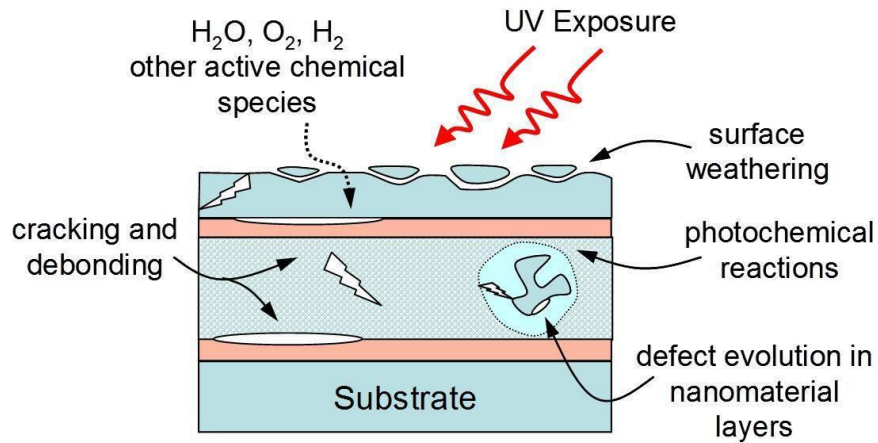
Figure 2.1: Degradation of FRP composite due to UV radiation exposure

2.2   Moisture Ingression in FRP composites

Polymer matrix has a high affinity for moisture. Degradation induced by moisture in FRP composites is the result of three fold damage occurring in fibers, polymer matrix and the interface. Fibre-matrix interface is the pathway for the fast diffusion of water into the matrix (polymer) of the composites [9]. Capillary action which is also known as water wicking is the main mechanism of diffusion and occurs predominantly in the composites in which wetting of the fibre by the matrix is not proper or incomplete [10]. Behaviour of transport of voids present in the matrix and fibre/matrix interphase can have significant effect on all round diffusivity of composite materials. A greater diffusion coefficient value for interphase than that of matrix has been suggested [11].

Absorption of water results in presence of water molecules in between polymer chains which increases its free volume and interrupts the Van der Waals bonding between polymer chains [12]. This phenomenon is known as Plasticization. Plasticization process has been schematically described in **Figure 2.2**, which is the result of interaction of polymeric chains with water molecules. These interactions hinder the hydrogen bonds existing in the polymer matrix [13] and cause the formation of new hydrogen bonds with the polymer. Plasticization has a negative effect on the properties of the polymer composite by induced some amount of matrix plastic deformation and by lowering the glass transition temperature. Plasticization reduces matrix strength, modulus, strain to failure and toughness.
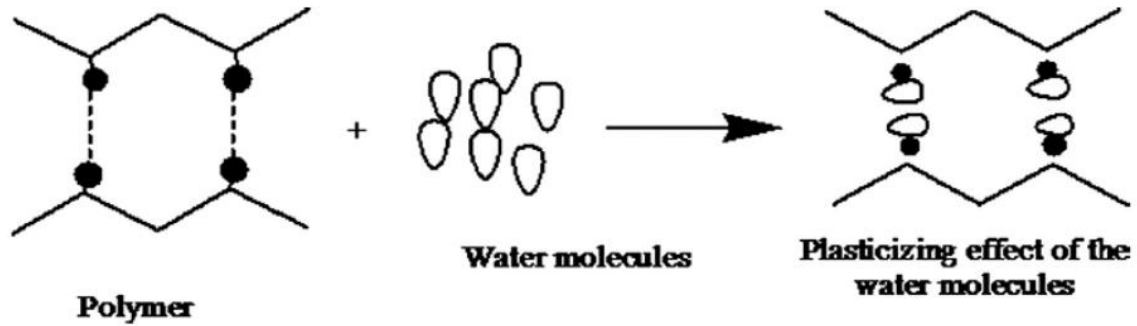
Figure 2.2: Plasticization caused by water molecules in polymer matrix

Water absorption causes increase in bond-length between polymer chains which results in swelling of the matrix and causes many irreversible damage through fibre-matrix debonding and matrix cracking. Formation of microvoids in the matrix polymer and at the interface is generally due to accumulation of water molecules [14]. By absorbing water, the swelling can result in internal stresses in the polymer, which may lead to formation of micro-cracks or microvoids. On the other hand, swelling due to moisture absorption may also relieve some of the residual stresses which had developed during the curing process [15].

In addition, physico-mechanical and chemical (hydrolysis and debonding) phenomena (micro-void and micro-crack propagation and formation) may occur in the composite, which can result in degradation of fibers, matrix, and the interface between them. Plasticization and swelling come under the category of reversible phenomenon, whereas hydrolysis, polymer relaxation, leaching, micro-cracking and microvoids formation are irreversible type of processes. Hydrolysis is known as the phenomena in which side chains get detached from the polymeric backbone chain. Even though some consider it to be an irreversible degradation mechanism [16], some other authors have reported that it is possible to reverse the hydrolyzing effect of diffusion of water molecules. Another mechanism known as leaching which involves break down of the interfacial region occurs and fibers and polymer get divided [17].

Moy et.al [18] has experimental work showed that in case of highly cross-linked epoxy resins moisture absorption is less as compared to than low cross-link density epoxy resins.

For many thermoset composites, the intake of moisture enhances the strength and stiffness but in contrast; for thermoplastic composites experimental resulted show no significant effect of moisture on both longitudinal and transverse mechanical properties [19].

Hygrothermal ageing indicates the simultaneous ageing under moisture and temperature environmental conditions which can damage the polymeric matrix [20]. Temperature related damages can further accelerate the moisture intake. For various orientation like symmetric and anti-symmetric GFRP laminates, decrease in flexural stiffness were found to be 54% and 27% respectively, when exposed to 98% RH humid environment for 2000 h [21].

2.3   Dynamic Mechanical Analysis of Thermo mechanical properties of FRP composites

Dynamic mechanical measurements observed over a range of temperatures provide valuable insight into the morphology, viscoelastic behaviour and structure of composites. Dynamic Mechanical Analysis measures the various properties of materials especially the mechanical properties as function of temperature, frequency and time and also it is a thermal analysis by which the various responses of a sample subjected to a definite temperature range are found out under certain periodic stress. DMA measurements explain how a material behaves at the moment and future [22].

DMA applies certain sinusoidal deformation to a sample whose geometry is known to us. The sample is subjected to either a controlled strain or a controlled stress. DMA measures damping and stiffness, which are referred to as tan delta and modulus. As a force of sinusoidal nature is applied, we can express the modulus as the storage modulus which is the in-phase E' is measured as the sample's elastic behaviour. The ratio of loss to storage modulus is tan delta and this is known as damping which measures loss of energy of a material [23].

The glass transition temperature, also called as a-transition in case of amorphous polymers, is the temperature at which loss of energy reaches a maximum value, as seen in DMTA analysis. Pothan et al. concluded that maximum peak width is observed for composites with highest fiber content [24]. Heitor Luiz Ornaghi Jr. showed that there was an increment in the storage and loss modulus as well as a shift to higher values for higher glass loading and all round fiber volume [25].

Thostenson et al. experimental work showed that tensile behaviour of aligned as well as random nanocomposites using DMTA where they observed that aligned nanotubes have better mechanical properties than random orientation of polymeric composites [26]. Manchado et al. showed the effect of SWNT concentration on physical and thermal

properties of iPP using tensile and DMTA tests [27]. Zhang et al. studied from DMTA studies that the mechanical properties are enhanced by the incorporation CNT in the composites [28]. Goh et al. found out the storage modulus of CNT composites within a range of temperature from -1000°C to 500°C and observed a significant improvement over the polymer properties [29]. Jin et al. made some CNT-PMMA composites and examined their mechanical properties from which it was indicated that storage modulus is enhanced by addition of nanotubes at very high temperature [30]. Gong et al. used surfactant as one of the processing means to improve the thermo mechanical properties of CNT-polymer composites [31]. Frederico Muylaert Margem conducted DMA tests and made a study of the variation of temperature with parameters mainly the dynamic-mechanical of the epoxy matrix composites introduced with up to a 30% in volume of the ramie fiber (**Figure 2.3**) [32].
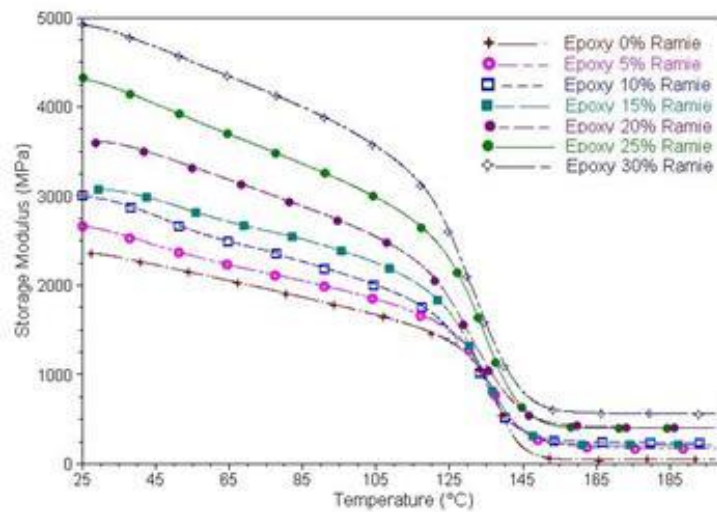
Figure 2.3: DMA Curves showing the variation of the storage modulus with temperature for pure epoxy and composites reinforced with different volume fractions of the ramie fibers.

[17]

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Materials

- Glass Fibers (FGP, RP-10)

- Epoxy Resin (Lapox L-12) based on Bisphenol A

- Hardener (Lapox K-6, AH-312)

- MWCNTs having an outer diameter of 6-9 nm with 5 μm length, purchased from Sigma-Aldrich.

Properties	Glass Fibers	Epoxy resin
Density (g/cc)	2.58	1.162
Tensile Strength (GPa)	3.4	0.11
Tensile Modulus (GPa)	72.3	4.1
Poisson's ratio	0.2	0.3
Strain at failure (%)	4.8	4.6
CTE (per million per C)	5	1.5-10

Table 3.1: Properties of Glass fibres (reinforcement) and Epoxy resin (matrix)

3.2 Fabrication of GE and CNT reinforced GE specimens

3.2.1 Fabrication of GE specimens

- Specified amount of hardener (10 wt. % of epoxy) was blended and stirred properly in the epoxy.

- Matrix and fibers were approximately in 2:3 proportion by weight.

- The laminates were prepared by hand lay-up process using 14 layers of woven fabric E-glass fibres. Curing was done at 60°C temperature and 10 kg/cm^2 pressure in a hot press for 20 minutes.

- The laminates were allowed to keep at room temperature for 24 hrs. Flexural (as per ASTM D7264), ILSS (as per ASTM D2344), and DMA samples were cut from the prepared laminates with a diamond cutter. Then the samples were post-cured at 140 °C for 6 hr.

3.2.2 Dispersion of MWCNT into epoxy resin

- In order to commence the hand layup fabrication process, it was needed to have MWCNT fused glass/epoxy (CNT-GE) composite which was done by modifying the epoxy resin by incorporating MWCNT to it.

- The amount of CNT in CNT-GE composite was varied as different compositions, like 0.1 wt.%, 0.3 wt.% and 0.5 wt.% of epoxy. Three different laminates were fabricated using these different compositions.

- Required amount of CNT was dispersed in 150mL of acetone.

- This suspension was stirred for 30 minutes at 1000 rpm using magnetic stirrer.

- Sonication of this suspension was done for 30 minutes. The purpose of stirring and sonication is to deagglomerate the existing agglomerates of CNTs.

- This CNT/acetone mixture was added to pre-weighed epoxy, which was brought to sufficient fluidity by heating.

- Further, stirring of epoxy/CNT/acetone mixture was done at 1000 rpm for 2 hours at 70°C and Sonication was again carried out at 70°C for 1 hr. At this stage, evaporation of all acetone was assured.

- The left epoxy/CNT suspension was vacuumed for 12 hours for the removal of air bubbles entrapped in the suspension during earlier stages.

(A)   (B)

Figure 3.1: A) Dispersion of CNT/epoxy at 100°C using magnetic stirrer at 1000 rpm, B) Sonication of CNT/epoxy dispersion at 70°C for one hour to further remove any agglomerates present.

[19]

3.2.3 Fabrication of Fiber reinforced nano-composites

- Specified amount of hardener (10 wt. % of epoxy) was blended and stirred properly in the epoxy/CNT suspension.

- Matrix and fibers were approximately in 2:3 proportion by weight.

- The laminates were prepared by hand lay-up process using 14 layers of woven fabric E-glass fibres. Curing was done at 60 °C temperature and 10 kg/cm^2 pressure in a hot press for 20 minutes.

- The laminates were allowed to keep at room temperature for 24 hrs. Flexural (as per ASTM D7264), ILSS (as per ASTM D2344), DMA samples were cut from the prepared laminates with a diamond cutter. Then the samples were post-cured at 140°C for 6 hr.

3.3 Exposure environments

3.3.1 UV Exposure

Post cured samples (both GE and CNT Reinforced GE) of specific dimensions for Short beam shear test and DMA analysis as per the ASTM standards were exposed to UV-C radiation in a UV chamber of 6 W power source for 500 hours. The temperature in the UV Chamber during the exposure period was maintained at around 50°C.

3.3.2 Humidity Conditioning

Post cured samples (both GE and CNT Reinforced GE) of specific dimensions for Short beam shear test and DMA analysis as per the ASTM standards were exposed in a Humidity chamber maintained at 95% RH and 60°C for 200 hours.

3.3.3 Hot Water Conditioning

Post cured samples (both GE and CNT Reinforced GE) of specific dimensions for Short beam shear test and DMA analysis as per the ASTM standards were dipped in hot water maintained at 60°C in a Humidity chamber for 200 hours.

3.3.4 Isothermal Holding

Post cured samples (both GE and CNT Reinforced GE) of specific dimensions for DMA analysis as per the ASTM standards were tested in three point bend mode at a frequency of 1 Hz. Isothermal holding was done at 90°C and 110°C for holding time of 30 min, 60 min, 3 hours and 6 hours.

3.4 Short Beam Shear Test

Short Beam Shear tests were being performed using Instron 5467 tensile testing machine according to ASTM D3039 and ASTM D2344-84 standards at ambient temperature. All the control samples as well as exposed samples were loaded at a rate of 1mm/min. In the similar manner, many samples (usually 3) were tested during the experiment and the average value was found.

3.5 Dynamic Mechanical Analysis

Post cured samples (both GE and CNT Reinforced GE) in a three point bend mode of specific dimensions for DMA analysis as per the ASTM standards were tested at a frequency of 1 Hz. The heating range was $+40^{\circ}$C to $+200^{\circ}$C with a heating rate of 5K/min.

3.6 Micrograph Study

Micrographs of fractured GE and CNT Reinforced GE specimens were obtained using FESEM at 10kV under various magnifications of 1000X, 2000X, 5000X and 10000X for their fracture analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Effect of addition of CNT on Flexural Strength and ILSS of FRP composites
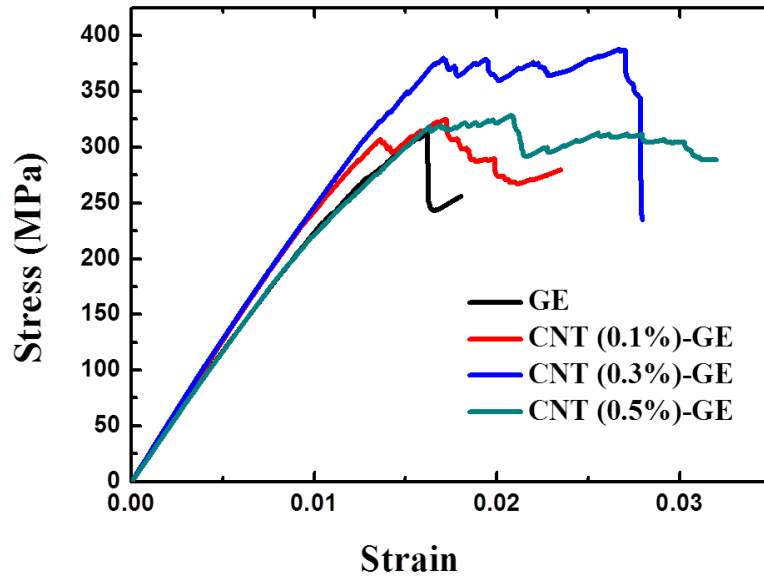
Figure 4.1: Stress vs. Strain curves for GFRP and CNT embedded GFRP composites
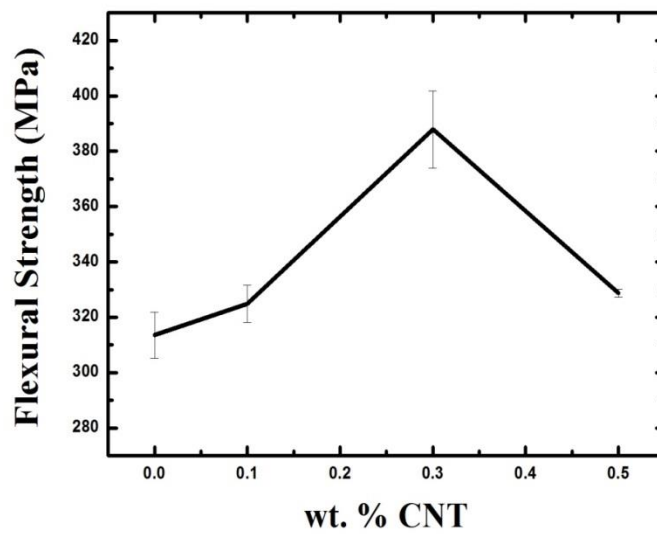
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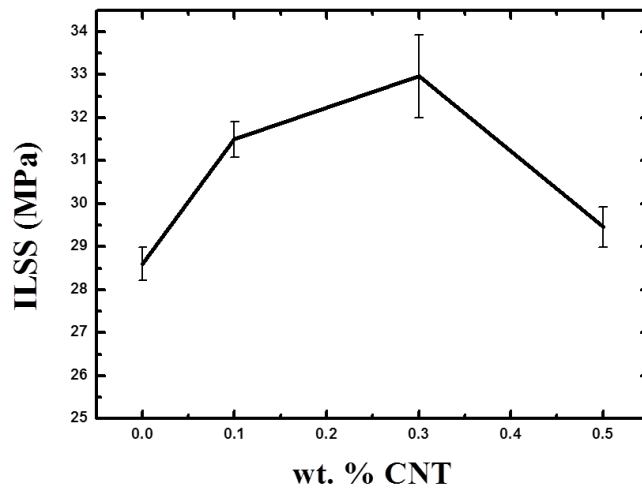
(B)

Figure 4.2: Variation of A) Flexural Strength and B) ILSS with wt. % CNT reinforced in GFRP composites

As evident from the above results, the flexural strength and ILSS of GFRP composite is found to increase on adding CNT up to 0.3 wt.% and decrease on further addition of CNT. Addition of 0.1wt% CNT, 0.3wt% CNT increased the flexural strength by 3.6% and 23.7% and increased the ILSS by 10.1% and 15.3% respectively. The low volume fraction of filler and its uniform dispersion improved the interfacial properties of fiber/matrix and enhanced the load transfer via matrix to the fibers. The decrease in mechanical properties at higher wt.% CNT is due to the agglomeration and hence a non-uniform dispersion of CNT in the matrix which decreases the interfacial area.

4.2   Dynamic Mechanical Analysis of addition of CNT in FRP composites
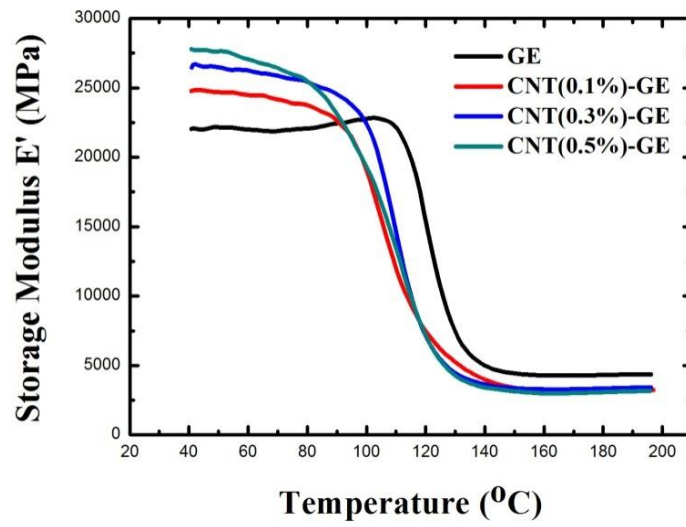
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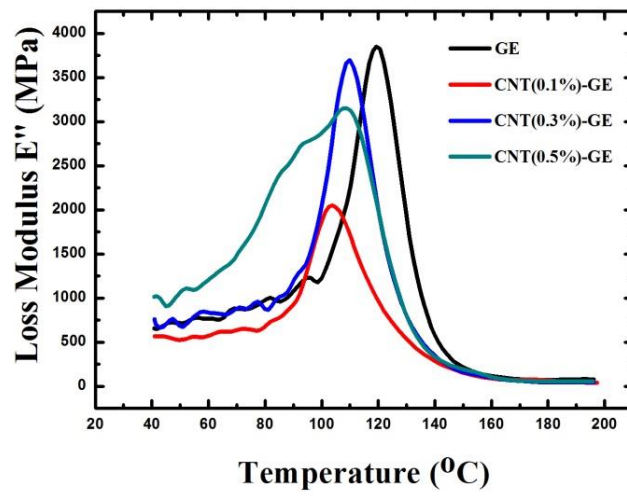
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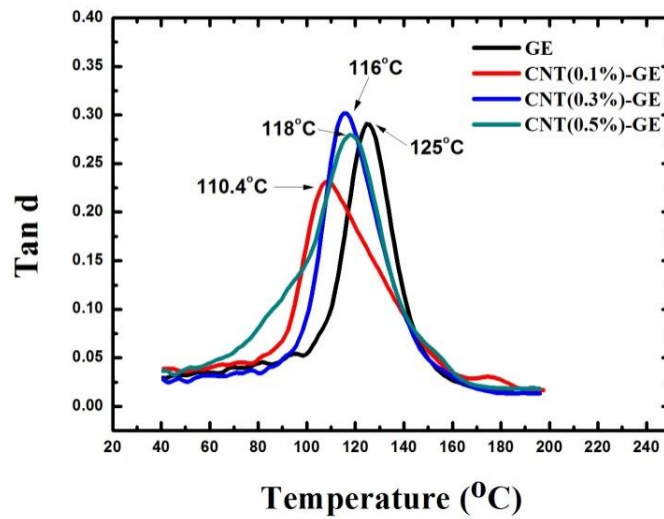
(C)

Figure 4.3: DMA curves showing A) Storage modulus vs. Temperature, B) Loss modulus vs. Temperature, C) Tan delta vs. Temperature for various CNT-GE systems

As evident from the curve, the Storage Modulus (E') increases with increasing wt.% CNT in GFRP composite. The increase is due to strengthening effect of CNTs by improving the interfacial properties of fiber/matrix and enhanced the load transfer via matrix to the fibers.

Similarly, the Loss modulus is highest for GE system. It decreases maximum in case of CNT(0.1%)-GE and lesser in case of CNT(0.3%)-GE and CNT(0.5%)-GE. This shows that loss of energy or damping is less in case of uniformly dispersed CNT reinforced composite.

The Glass Transition temperature was found from the peak of tan delta curves. The T_g of GFRP is 125°C. On adding CNT, T_g is found to decrease because of the presence of CNT particles in the polymeric matrix which hampers the cross linking between polymer chains. The decrease is maximum for 0.1wt%CNT-GE system due to uniform dispersion of CNT and presence of voids in the matrix. The decrease in T_g is lesser in case of 0.3wt%CNT-GE and 0.5wt%CNT-GE systems due to agglomeration of nanoparticles.

4.3   Effect of various exposure environment on Flexural Strength and ILSS of FRP composites
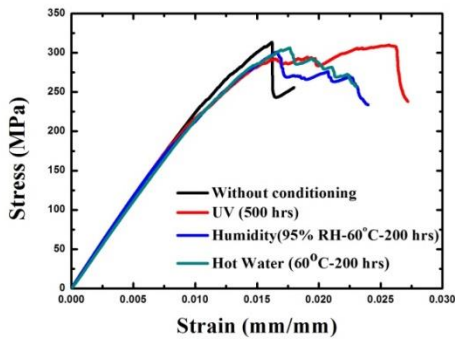
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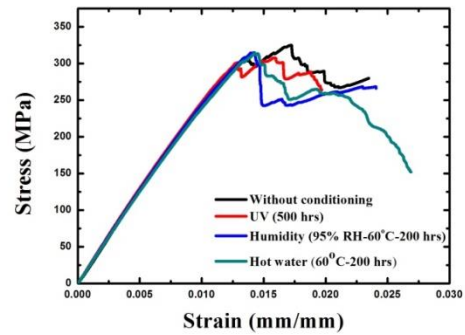
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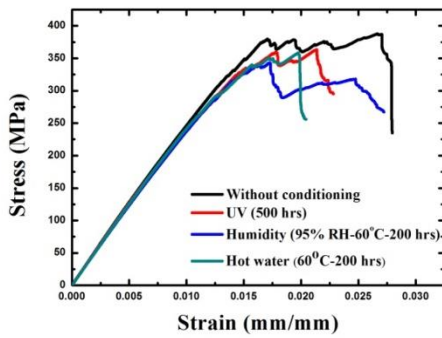
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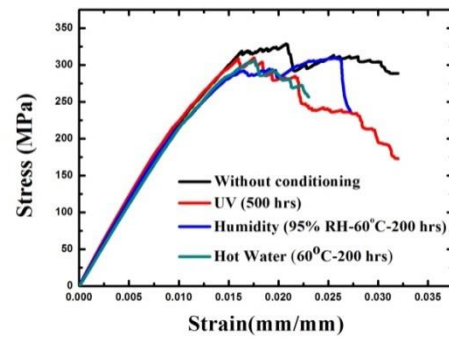
(D)

Figure 4.4: Stress vs. Strain curves for A) GE, B) CNT(0.1%)-GE, C) CNT(0.3%)-GE and D) CNT(0.5%)-GE under various environmental exposures
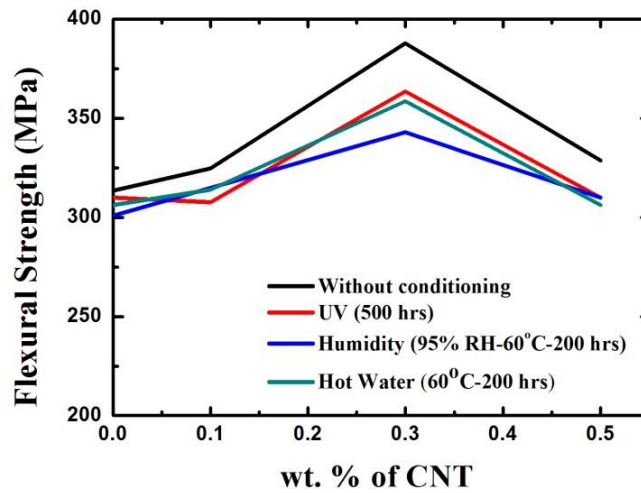
Figure 4.5: Variation of Flexural Strength with wt.% CNT in GFRP composite under various cases of conditioning
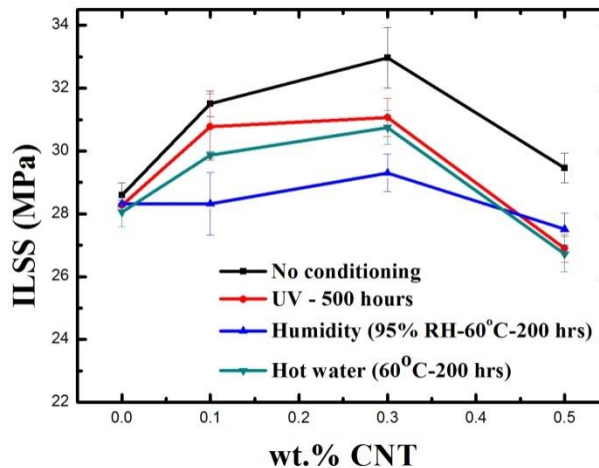

Figure 4.6: Variation of ILSS with wt. % CNT in GFRP composite under various cases of conditioning

As evident from above graphs, the flexural strength and ILSS decreases on exposing the CNT-GE systems to:

- 500 hours of UV radiation which resulted in chemical bonds breaking giving rise to many free radicals, oxidative loss, which resulted in permanent chain scission.
- 95%RH and 60°C humid environment for 200 hours due to the absorbed moisture causing the fiber/matrix interface to become susceptible to aggressive reactions which

result in change in interfacial chemistry, thereby affecting its load transfer characteristics and structural integrity

- Hot water at a temperature of $60^{o}C$ in which water absorption resulted in matrix swelling but swelling of the composite lamina is prohibited in fiber direction and some amount of residual stresses are introduced in multidirectional laminate.

It is observed that the mechanical properties are degraded most on exposure to 95%RH-$60^{o}C$ humid condition and least under UV radiation.

It is also observed that the decrease in mechanical properties increased with increase wt. % CNT in GFRP composite. This is because amount of moisture and water absorption increases with increase amount of CNT dispersed in the composite as can be understood from **Figure 4.7** given below. This is because presence of CNT particles creates voids in the matrix which increases moisture absorption.
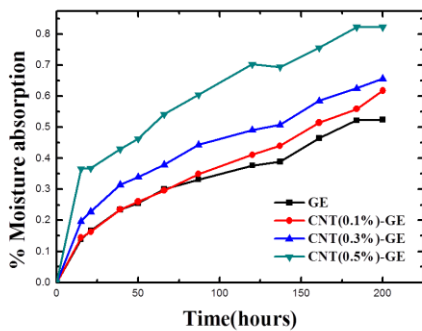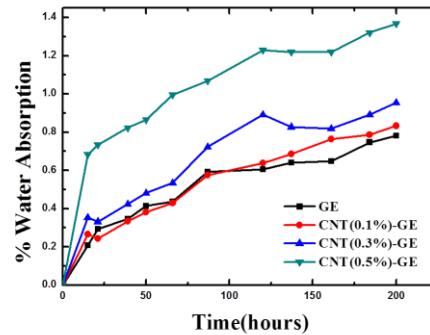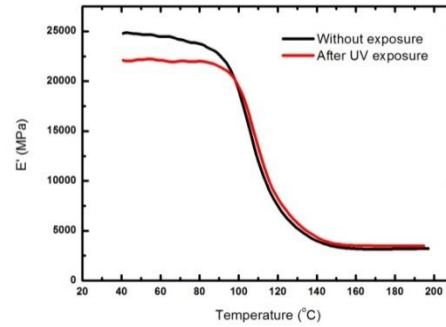

(A)   (B)

Figure 4.7: Variation in A) % moisture absorption, B) % water absorption with wt. % CNT in GFRP composites
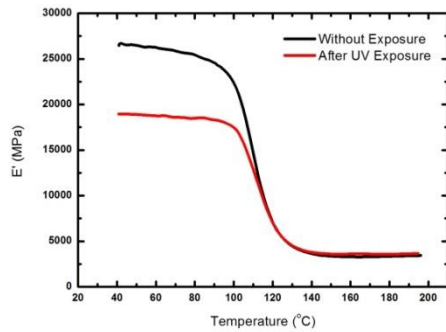
4.4 Dynamic Mechanical Analysis of various environmentally exposed FRP composites
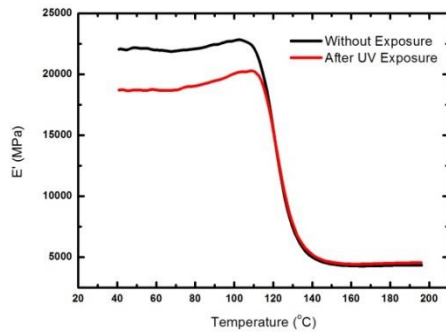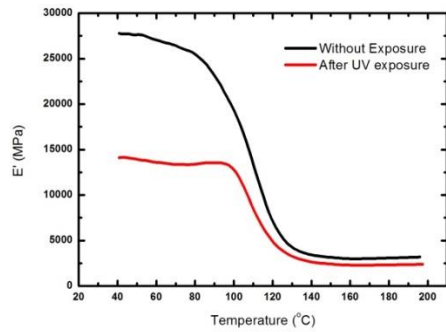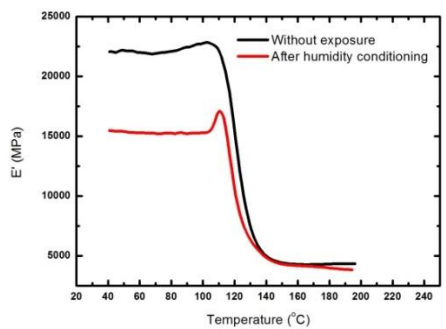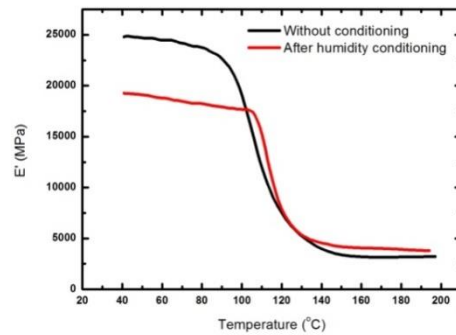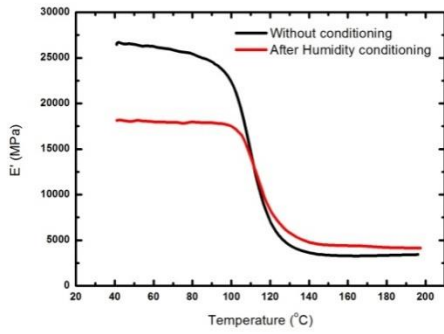

(A)   (B)

(C)   (D)

Figure 4.8: DMA curves of A) GE, B) CNT(0.1%)-GE, C) CNT(0.3%)-GE, D) CNT(0.5%)-GE before and after UV Exposure
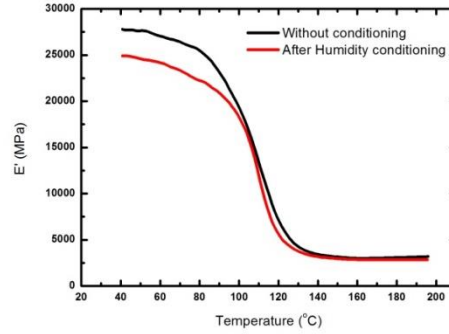

(A)   (B)

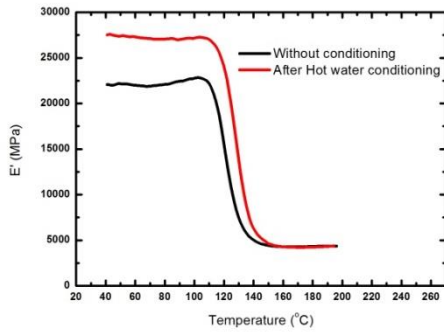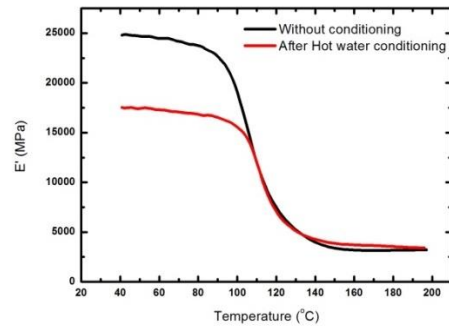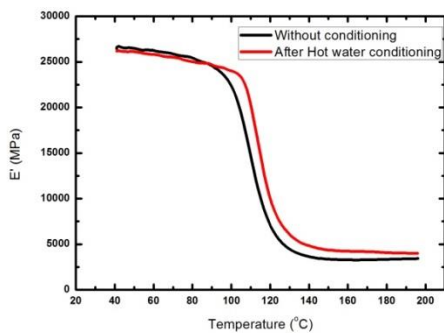(C)   (D)

Figure 4.9: DMA curves of A) GE, B) CNT(0.1%)-GE, C) CNT(0.3%)-GE, D) CNT(0.5%)-GE before and after Humidity (95% RH-60°C-200 hrs) conditioning

(A)   (B)
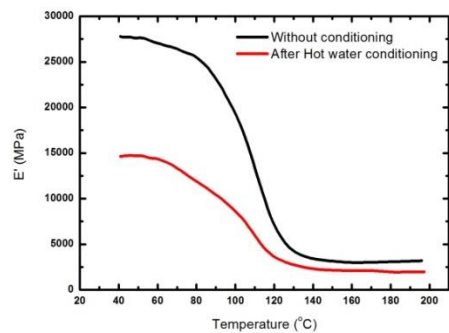

(C)   (D)

Figure 4.10: DMA curves of A) GE, B) CNT(0.1%)-GE, C) CNT(0.3%)-GE, D) CNT(0.5%)-GE before and after Hot Water (60°C-200 hrs) conditioning

As evident from above DMA curves, there is seen a significant decrease in the storage modulus of the composites in all the three cases of conditionings. In case of UV and humidity exposure, the degradation in modulus value decreased on addition of 0.1wt.% CNT in GFRP composite in the composite due to better interfacial adhesion. For hot water conditioning, the degradation was least for 0.3%wt CNT-GE composite as its uniform dispersion increased the resistance to water absorption. Degradation increased for 0.5wt% CNT-GE system due to agglomeration of CNTs in the matrix.

(A)

(B)

[31]
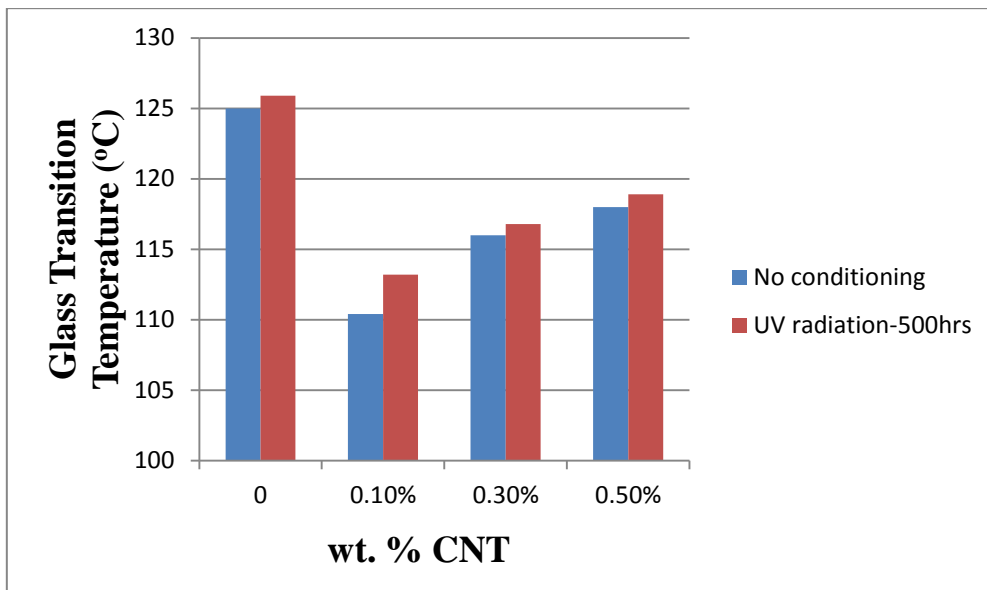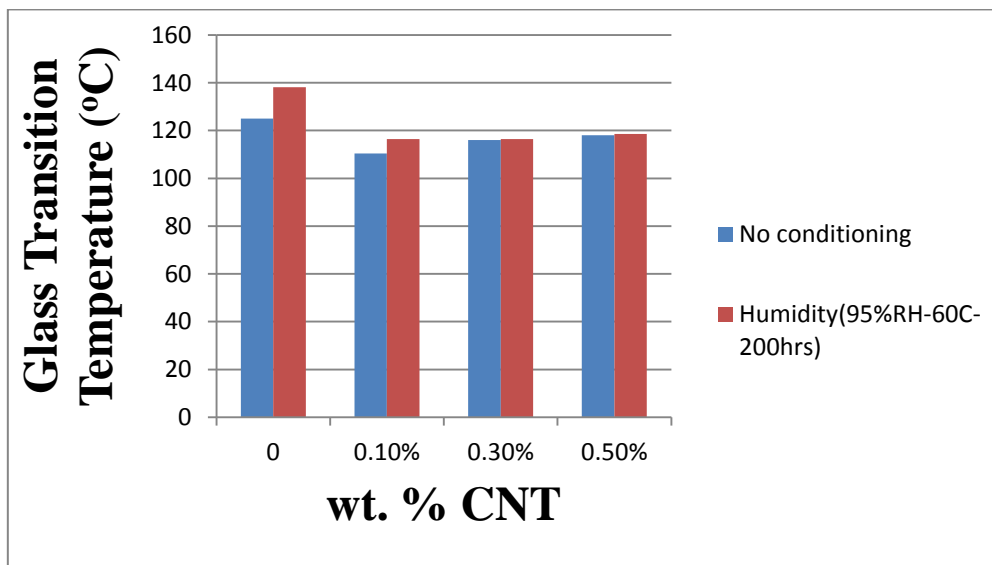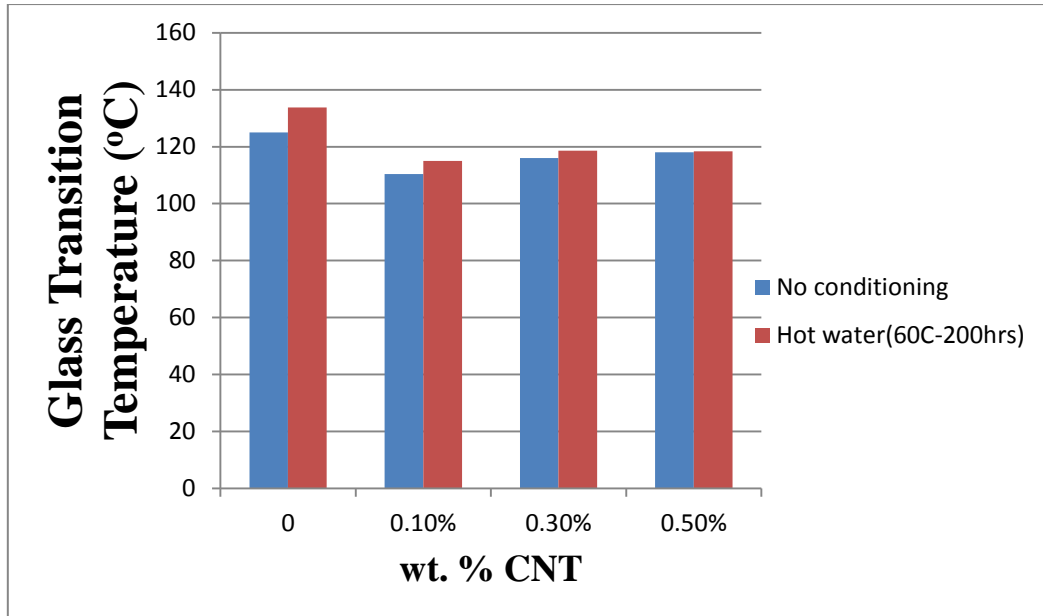
(C)

Figure 4.11: Variation of Glass Transition Temperature with wt. % CNT in GFRP composites under A) UV exposure-500hrs, B) Humidity (95%RH-60°C-200hrs), C) Hot water(60°C-200hrs) conditioning

It is observed that:

- On exposing the composite to 500 hours of UV radiation, the Glass Transition temperature (T_g) showed a slight increase due to the curing action of UV light.
- Short term exposure to humid and hot water environment resulted in slight increase in T_g due to swelling of composites on absorption of moisture and removal of internal stresses which are produced during curing.

Variation of T_g with wt. % CNT on exposure environment is similar to that of without exposure. 0.1 wt% CNT-GE system shows a larger drop in T_g temperature with respect to GE due to uniform dispersion of CNTs which hampers cross linking whereas at higher wt.% CNT(0.3%,0.5%) the T_g value decreases less due to increase in agglomeration of CNTs which restricts movement of polymeric chains.

4.5 Effect of Isothermal Holding on Thermo mechanical properties of FRP composites
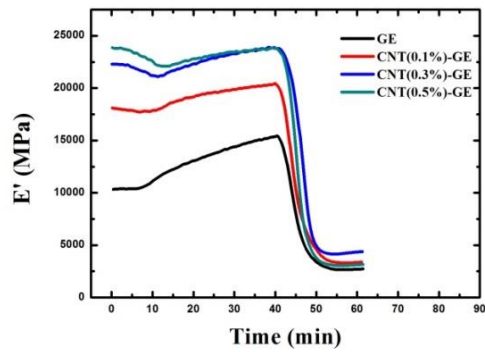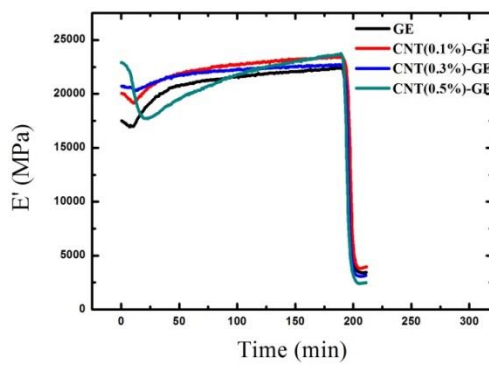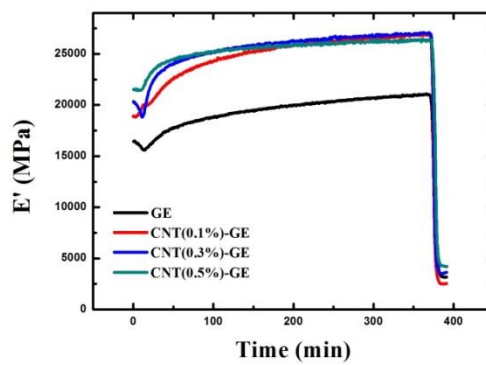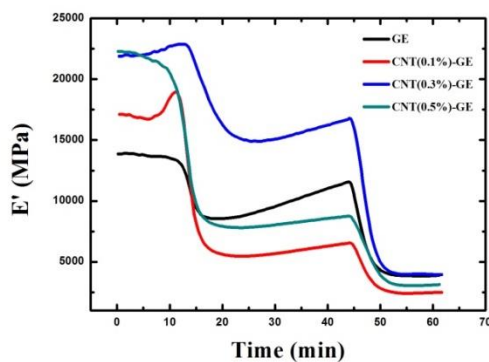

(A)
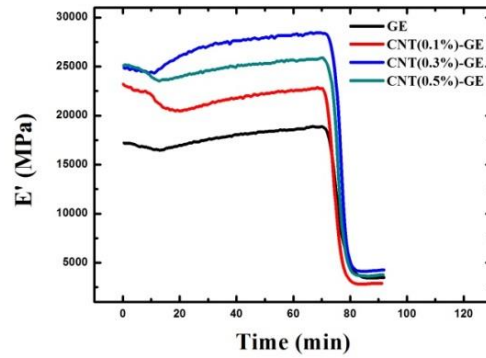
(B)

(C)

(D)

Figure 4.12: DMA curves of GE and CNT-GE composites for isothermal holding at 90°C for A) 30 mins, B) 60 mins, C) 3 hours, D) 6 hours

(A)

(B)

[33]
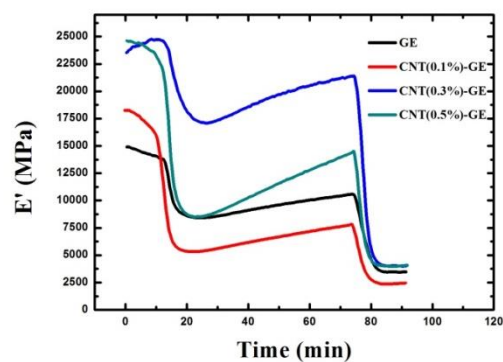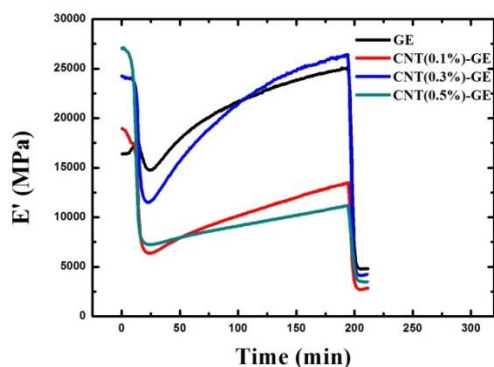
(C)
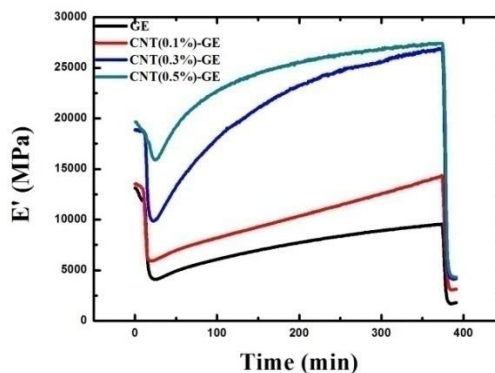
(D)

Figure 4.13: DMA curves of GE and CNT-GE composites for isothermal holding at 110°C for A) 30 mins, B) 60 mins, C) 3 hours, D) 6 hours
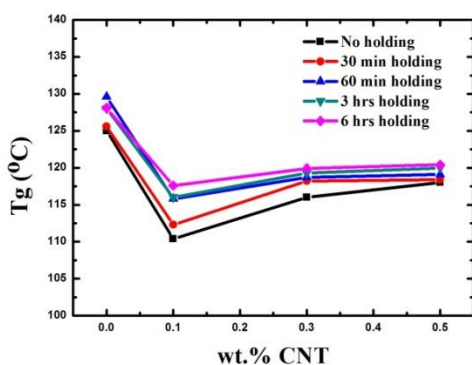
(A)
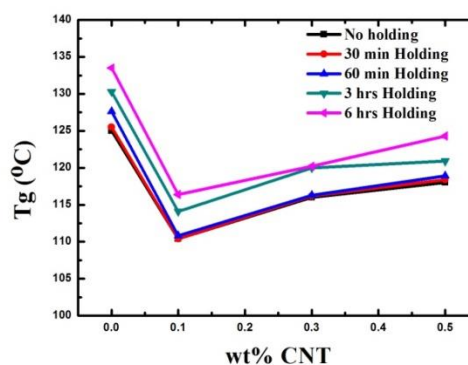
(B)

Figure 4.14: Variation of Glass Transition temperature with holding time for different CNT-GE systems at isothermal holding temperature of A) 90°C, B) 110°C

For isothermal holding at 90°C before Tg, there is slight increase in Modulus as can be seen from the increasing slope of the isothermal region. The glass transition temperature is also found to increase with increasing holding time. This is due to the removal of residual stresses introduced during the curing process. In case of holding at 90°C for various time period not much change in the modulus and glass transition temperature is observed.

For isothermal holding at 110°C just before Tg, there is an initial drop in the modulus value due to glass transition but gradually a significant increase in modulus is observed. In this

case, the glass transition temperature also shows a higher increase with holding time as compared to isothermal holding at 90°C. This increase is attributed to:

- Removal of residual curing stresses in the matrix
- Deagglomeration of CNTs due to holding at high temperature which induced better interfacial properties
- Enhanced crosslinking of polymeric chains due to increased interfacial area

4.6   Failure Analysis of GE and CNT-GE composite systems
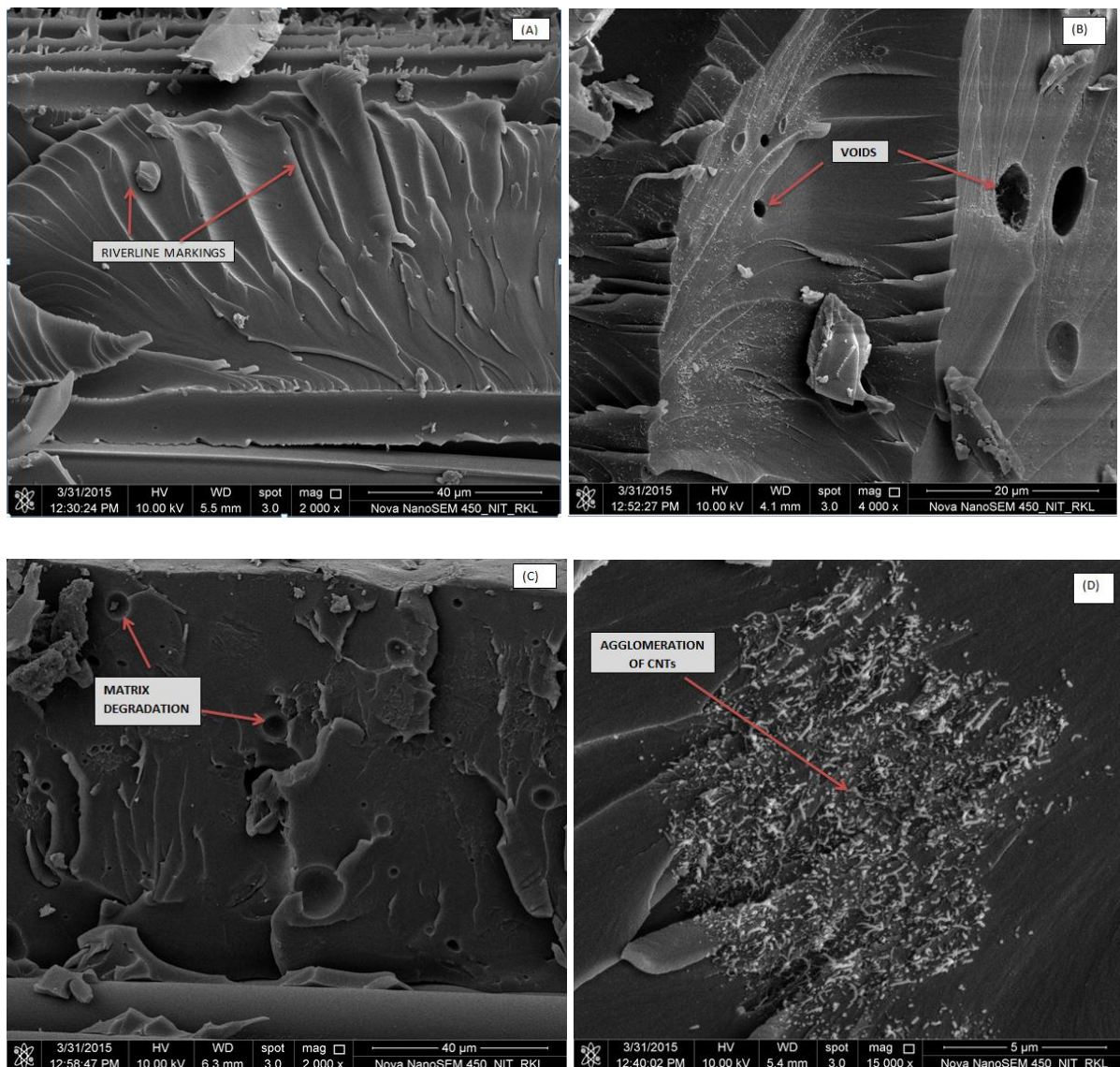
Figure 4.15: Micrographs of fractured surfaces obtained using field emission scanning electron microscope (A) GE Composite tested at ambient temp, (B) CNT(0.1%)-GE composite tested at ambient temp, (C) CNT(0.3%)-GE composite tested at ambient temperature (D) CNT(0.5%)-GE composite tested at ambient temperature

[35]

After 3 point bend test, analysis of fractured surfaces was done under FESEM to study various mechanisms of failure.

- Figure 4(a) shows the fracture surface of GE composite done at room temperature. Riverline markings are observed. Riverlines are most important features in predicting crack growth prevalent in brittle matrix systems. Convergence direction of "riverlines" helps us to predict the direction of crack growth in the crack planes.

- Figure 4(b) shows the fracture surface of CNT(0.1%)-GE composite tested at room temperature. This specimen is characterised by presence of microvoids which were the main cause of failure as it led to non-uniform dispersion of CNT.

- Figure 4(c) shows the fracture surface of CNT(0.3%)-GE composite tested at room temperature. The failure of matrix is clearly visible and its cause may be due to the higher interfacial strength of glass fibers with epoxy resin.

- Figure 4(d) shows the fracture surface of CNT(0.5%)-GE composite tested at room temperature. In this, we can observe chunks of agglomerated CNTs in the matrix which degraded the interfacial bonding and hence its properties.

CHAPTER 5

CONCLUSION

The effect of CNT addition to GFRP composite, UV irradiation, Hot water and humidity conditioning as well as isothermal holding at high temperatures was studied for GE and various CNT-GE systems. The following conclusions can be addressed from the present project work:

- Addition of 0.1wt% CNT, 0.3wt% CNT increased the flexural strength by 3.6% and 23.7% and increased the ILSS by 10.1% and 15.3% respectively because of enhanced interfacial properties whereas adding 0.5wt% CNT decreased those properties due to CNT agglomeration. Storage modulus is found to increase with increasing CNT content. Glass transition temperature decreased on adding CNT to the polymer matrix due to presence of CNT in between polymeric chains which hampers the cross-linking.

- UV exposure degraded the flexural strength, ILSS as well as storage modulus of the composite systems due to breaking of bonds and chain scission. Due to the short term exposure, glass transition temperature is found to slightly increase on account of curing by UV light.

- Humidity as well as Hot water conditioning degraded the flexural strength, ILSS as well as storage modulus due to moisture ingression by the polymer and plasticization phenomenon. Glass transition temperature increased on short term exposure due to removal of internal curing stresses present in the composite.

- The Modulus as well as Glass Transition temperature is found to increase as the amount of holding time increases. This increment is much more significant in case of isothermal holding at $110^{o}C$ than at $90^{o}C$ due to increased deagglomeration of CNTs and removal of residual curing stresses.

- Study of FESEM fractographs showed riverline markings which showed brittle fracture mode of composites. 0.1wt% CNT-GE system showed presence of voids. 0.3wt% CNT-GE system had uniform dispersion of CNTs, hence the better mechanical properties. 0.5wt% CNT-GE system showed agglomeration of CNTs, hence the reason for poorer properties.

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