



**STUDIES ON THERMAL AND MECHANICAL PROPERTIES
OF CARBON NANOFIBER/MULTIWALL CARBON
NANOTUBES REINFORCED EPOXY ADHESIVE BASED
JOINTS**

**PROJECT REPORT
2015-16**

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CERTIFICATE

This is to certify that the report on “studies of thermal and mechanical properties of CNT reinforced epoxy adhesive based joints”. Vikram tomar and Vikram jaglan in the completion of the requirements for the award of degree of Bachelor of Technology in Material Science Engineering with specialization in Nano Technology from College of Engineering Studies is an original work carried out by them under our joint supervision and guidance.

It is certified that the work has not been submitted anywhere else for the award of any other diploma or degree of this or any other University.

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ACKNOWLEDGEMENTS

It gives us pleasure to express a sense of great indebtedness and sincere gratitude to our project guide D.r Manjeet singh goyat ,Department of physics, University of petroleum and energy studies, for his relentless support and enthusiasm throughout the Project work. It would have been impossible to materialize the concepts in the area of “**CNT/epoxy nanocomposites**”, without his invaluable guidance and spontaneity and much aspiration that led us to delve deeper into the issue.

We further thank M r. Amneesh Singla for monitoring and organizing our work. They always helped in providing the access to composite lab .

We are also thankful to Mr. Arun choudhary and Mr. Kaushal Chauhan, PhD Scholars, MMED for discussing their experience regarding carbon nanoforms, nanocomposites and adhesives. It would have been impossible to complete this project without their suggestions, moral support and constant encouragement during the course of this work.

ABSTRACT

Untreated and acid-treated multi-walled carbon nanotubes (MWCNTs) were fabricated using cobalt catalysed Chemical Vapour Deposition (CVD) process to prepare fillers for reinforcement of epoxy adhesive. Ultrasonic dual mode mixing (UDMM) process via ultrasonic vibration along with magnetic stirring was used to reinforce epoxy adhesive by CNTs. Epoxy nanocomposites containing 0.5, 1.0 and 2.0 wt% of untreated CNTs were produced. The untreated and treated CNTs were characterized using FESEM and EDAX analysis. The thermal and mechanical properties of untreated CNTs reinforced epoxy nanocomposite were studied using Differential thermal analyzer/Thermo-gravimetric analyzer (DTA/TGA) and FESEM. The thermal properties of neat epoxy and epoxy nanocomposites in terms of glass transition temperature (T_g), decomposition temperature and Integral procedural decomposition temperature (IPDT) were studied. The mechanical properties of neat epoxy and epoxy nanocomposites in terms of tensile strength, elastic modulus, fracture toughness and fracture energy were studied. The FESEM and EDX analysis of the carbon nanoforms show the presence of both carbon nanotubes (CNTs) and carbon nanobeads. The DTA/TGA studies revealed that CNTs reinforced epoxy nanocomposite can produce a 13 °C increase in T_g compared to the neat epoxy adhesive. The thermal stability and Integral Procedural Decomposition Temperature (IPDT) values also showed a steady increase till 2 wt% CNTs loading. The tensile test results showed that both tensile strength and elastic modulus increased with higher CNT loading percentage and showed the maximum strength enhancement for 2 wt% CNTs loading. The fracture toughness results showed a significant improvement in K_{IC} value for 1 wt% CNTs loading. The fracture surfaces of the nanocomposite samples were analyzed using FESEM.

TABLE OF CONTENTS

	<i>Page</i>
Candidate's Declaration	ii
Acknowledgements	iii
Abstract	iv
List of Figures	vii
List of Tables	ix
Chapter	
1.Introduction	1
2.Literature Review	2
1.1.....Carbon nanotubes	2
2.1.1 Types and properties	2
2.1.2 Preparation process	4
2.1.2.1. Arc Discharge	4
2.1.2.2. Laser Ablation	5
2.1.2.3. Chemical Vapor Deposition	5
2.2. Epoxy	6
2.2.1 Types and properties	6
2.2.2 Structural applications	7
2.3. Dispersion of carbon nanotubes	8
2.4. Mechanical properties of CNT/Epoxy composites	10
2.5. Thermal properties of CNT/Epoxy composites	14
2.6. Thermo-mechanical properties of CNT/Epoxy composites	15
2.7. Summary and Problem Statement	17
2.....Experimental Procedure	19
3.1. Objective	19
3.2. Chemicals used	19
3.3. Experimental setup	19
3.4. Procedure followed	19
3.4.1. Synthesis of CNTs	19
3.4.2. Synthesis of CNTs reinforced epoxy composites	20
3.5. Characterization by FESEM & EDAX	21
3.6. Mechanical property testing	21
3.7. Thermal property testing	23

3.....	Results and Discussions	25
4.1.	Microscopic characterization (FESEM and EDAX)	25
4.2.	Mechanical properties	32
4.2.1.	Tensile strength	32
4.2.2.	Elastic modulus	33
4.2.3.	Fracture toughness and energy	34
4.3.	Thermal properties	36
4.3.1.	Glass transition temperature	36
4.3.2.	Thermal stability	37
4.3.3.	IPDT	39
4.4.	Comparison with neat epoxy resin	42
4.....	Conclusion	43
5.....	References	46

LIST OF FIGURES

<i>Number</i>	<i>Description</i>	<i>Page</i>
2.1.	TEM image of a single walled carbon nanotube	3
2.2.	TEM image of a multi walled carbon nanotube	4
2.3.	Structure of DGEBA	7
2.4.	TEM image of partially exfoliated SWNT	8
2.5.	Tensile test stress-strain curve of the resin and its composites	14
2.6.	Glass transition temperature as a function of nanotubes content	16
2.7.	DMA measurements for anhydride-cured epoxy/FSWCNT nanocomposites	16
2.8.	Flowchart of proposed studies	18
3.1.	Process cycle of Ultrasonic Dual Mode Mixing	21
3.2.	Setup of Ultrasonic Dual Mode Mixing	21
3.3.	Tensile test specimen	23
3.4.	Fracture toughness test specimen	23
4.1.	FESEM image of catalyst for CNT preparation	25
4.2.	EDAX analysis of the catalyst	26
4.3.	FESEM image showing carbon nanotubes	27
4.4.	EDAX analyzing region around carbon nanotubes	28
4.5.	EDAX showing elemental analysis of the CNT tip	29
4.6.	FESEM image of a certain batch of clean carbon nanoforms sample showing a high amount of nanobeads	30
4.7.	FESEM image of fracture surface of 0.5, 1 and 2 wt % unclean CNT/epoxy nanocomposites respectively at two different magnifications	31
4.8.	Plot of tensile strength vs. filler wt % for unclean CNT/epoxy nanocomposites	32
4.9.	Plot of elastic modulus vs. filler wt % for unclean CNT/epoxy nanocomposites	34
4.10.	Plot of fracture toughness against filler wt % (unclean CNTs)	35
4.11.	Plot of fracture energy against filler wt % (unclean CNTs)	35
4.12.	Figure showing Tg calculation of a 0.5 wt% clean CNT/apoxy nanocomposite	36
4.13.	Plot showing variation of glass transition temperature against both unclean and clean CEN	37
4.14.	Plot of different decomposition temperatures vs. filler wt % of	

	unclean CEN	38
4.15.	Plot of different decomposition temperatures vs. filler wt % of clean CEN	39
4.16.	The schematic diagram of Doyle's method for determining IPDT	40
4.17.	IPDT variation with filler wt % of unclean and clean CNT /epoxy Nanocomposite	41

LIST OF TABLES

<i>Number</i>	<i>Description</i>	<i>Page</i>
2.1.	Comparison of mechanical properties	4
2.2.	Properties of neat epoxy resin	7
2.3.	Processing parameters of nanocomposites	9
2.4.	DMA results of SWCNT/SC-15 nanocomposites	10
2.5.	Mechanical properties of nanoparticle reinforced composites	13
4.1.	Tensile strength values of unclean CNT/epoxy nanocomposites	32
4.2.	Elastic modulus values of unclean CNT/epoxy nanocomposites	33
4.3.	Variation of fracture toughness and fracture energy of unclean CNT/epoxy nanocomposites	34
4.4.	Average values of Tg of both unclean and clean CNT/epoxy nanocomposites	36
4.5.	Values of different decomposition temperatures against their respective nanocomposite samples	38
4.6.	IPDT values of different nanocomposite samples	41
4.7.	Properties of neat epoxy resin along with maximum properties shown by the CEN	42

CHAPTER 1

INTRODUCTION

Composites are defined as a material consisting of two or more physically and/or chemically distinct and suitable arranged with a separating interface whose characteristics are not depicted by any of the components in isolation. The aim of developing a composite is combine materials with objective of getting more desirable combination of properties. Carbon nanofibers and nanotubes are promising to revolutionize several fields in material science and are a major component of nanotechnology. Carbon nanotubes posses a variety of useful properties like excellent mechanical strength, thermal and electrical conductivity which makes them a highly suitable as reinforcements in composites. Carbon nanotubes (CNTs) provide a large surface area for effective load transfer from matrix to reinforcement. Many of these outstanding properties can be best exploited by incorporating the nanotubes into some form of matrix, and the preparation of nanotube containing composite materials is now a rapidly growing subject. In many cases, these composites have employed polymer matrices, but there is also interest in other matrix materials, such as ceramics and metals. In our case of epoxy matrix the results of the investigation showed that nanotubes act as a strong catalyst and enhance the rate of cure reaction and also thermal degradation because of the higher thermal conductivity of the nanotubes which can be dispersed well in the matrix at low concentration. Carbon nanotubes have a tendency to form clusters in the matrix. If clusters are formed the effective interface area is reduced which then doesn't allow enhancement of properties. Therefore it is very important that these clusters are broken down and the dispersion is improved. There are various dispersion techniques being used which include high speed shear mixing calendaring, ultrasonication, use of solvent and surfactant etc. The aim of this report is to review recent work on carbon nanotubes epoxy composites, and to assess how successful this work has been in exploiting the full potential of nanotubes. In this regard efforts were made to understand the reported work regarding the utility of CNTs for its usage in preparation of epoxy based composite readily after its production or through any pre-treatment and the effectiveness of its dispersion in the resin.

CHAPTER 2

LITERATURE REVIEW

Since their discovery in 1991, extensive research has been carried out to understand and exploit the unique properties of CNTs in the form of composites for various applications. But the main challenge lies in transferring the properties of carbon nanotubes to the nanocomposites successfully. Keeping this in mind numerous research works regarding the method of production of CNTs , different treatment methods for better dispersion , homogenisation methods and their effective property changes brought by in the nanocomposites, have been reviewed. To begin, a brief introduction is given to the science of carbon nanotubes.

2.1. Carbon Nanotubes

Elemental carbon in the sp^2 hybridization can form a variety [1] of amazing structures. Apart from the well-known graphite, carbon can build closed and open cages with honeycomb atomic arrangement. The first such structure to be discovered was the C60 molecule by Kroto [2] *et al.*

Although various carbon cages were studied, it was only in 1991, when Iijima [3] observed for the first time tubular carbon structures. The nanotubes consisted of up to several tens of graphitic shells (so called multi-walled carbon nanotubes (MWNT)) with adjacent shell separation of 0.34 nm, diameters of 1 nm and high length/diameter ratio. Two years later, Iijima and Ichihashi [4] and Bethune[5] *et al.* synthesized single-walled carbon nanotubes (SWNT) (Figure 2.1).

2.1.1. Types and Properties

There are two main types of carbon nanotubes [6] that can have high structural perfection. Single walled nanotubes (SWNT) consist of a single graphite sheet seamlessly wrapped into a cylindrical tube. Multi-walled nanotubes (MWNT) comprise an array of such nanotubes that are concentrically nested like rings

of a tree trunk .

All nanotubes are expected to be very good [thermal conductors](#) along the tube, exhibiting a property known as "[ballistic conduction](#)", but good insulators laterally to the tube axis. Measurements show that a SWNT has a room-temperature thermal conductivity along its axis of about $3500 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$; compare this to copper, a metal well known for its good [thermal conductivity](#), which transmits $385 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. A SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about $1.52 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is about as thermally conductive as soil. The temperature stability of carbon nanotubes is estimated to be up to $2800 \text{ }^\circ\text{C}$ in [vacuum](#) and about $750 \text{ }^\circ\text{C}$ in air.

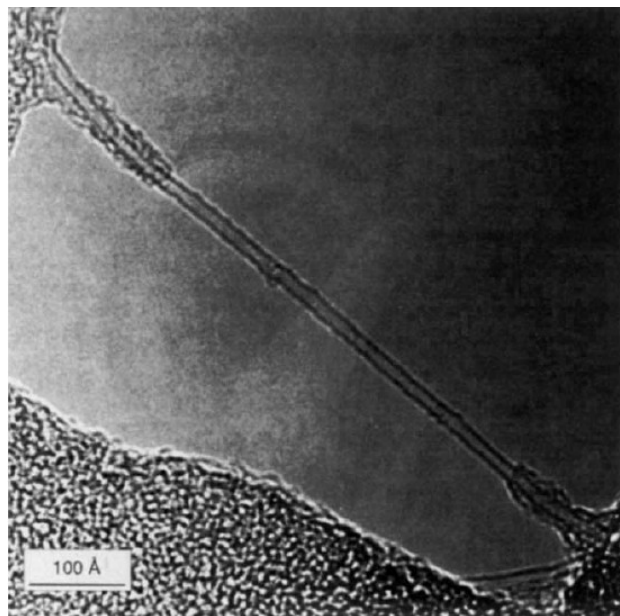


Figure 2.1. TEM image of a Single Walled Carbon Nanotube [5]

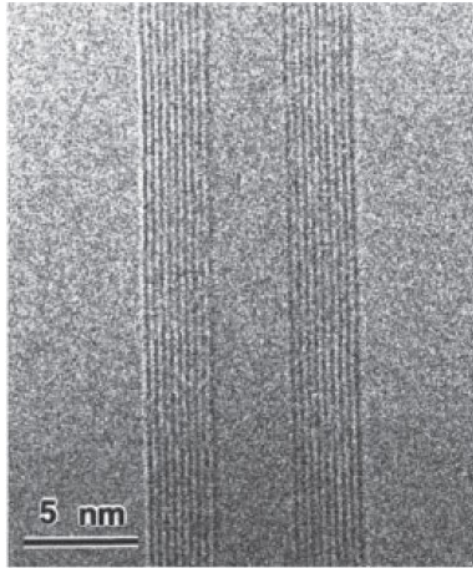


Figure 2.2. TEM image of a Multi Walled Carbon Nanotube [6]

Table 2.1. Comparison of mechanical properties [7]

Type	Young's Modulus(TPa)	Tensile Strength (GPa)	Elongation at break (%)
MWCNT	0.2-0.95	11-150	20-30

2.1.2. Preparation process

There are various techniques available to produce CNT's such as laser ablation, thermal and plasma enhanced chemical vapor deposition techniques, sol-gel technique, arc discharge etc.

2.1.2.1. Arc-Discharge

In 1991, Iijima reported the preparation of a new type of finite carbon structures consisting of needle-like tubes. The tubes were produced using an arc discharge evaporation method similar to that used for the

fullerene synthesis. The carbon needles, ranging from 4 to 30 nm in diameter and up to 1 mm in length, were grown on the negative end of the carbon electrode used for the direct current (dc) arc-discharge evaporation of carbon in an argon-filled vessel (100 Torr).

2.1.2.2. Laser Ablation

In 1996, Smalley and coworkers produced high yields (>70%) of SWNT by laser ablation (vaporization) of graphite rods with small amounts [7] of Ni and Co at 1200 °C. The tube grows until too many catalyst atoms aggregate on the end of the nanotube. The large particles either detach or become over-coated with sufficient carbon to poison the catalysis. This allows the tube to terminate with a fullerene-like tip or with a catalyst particle.

Both arc discharge and laser-ablation techniques have the advantage of high (>70%) yields of SWNT and the drawback that (1) they rely on evaporation of carbon atoms from solid targets at temperatures >3000 °C, and (2) the nanotubes are tangled which makes difficult the purification and application of the samples.

2.1.2.3. Chemical Vapor Deposition

Despite the described progress of synthetic techniques [8] for nanotubes, there still remained two major problems in their synthesis, i.e. large scale production and ordered synthesis. But, in 1996 a CVD method emerged as a new candidate for nanotube synthesis. This method is capable of controlling growth direction on a substrate and synthesizing [9] a large quantity of nanotubes. In this process a mixture of hydrocarbon gas, acetylene, methane or ethylene and nitrogen was introduced into the reaction chamber. During the reaction nanotubes were formed on the substrate by the decomposition of the hydrocarbon at temperatures 700–900°C and atmospheric [10] pressure. The process has many advantages: (1) the nanotubes are obtained at much lower temperature, although this is at the cost of lower quality (2) the catalyst can be deposited on a substrate, which allows for the formation of novel structures (3) cleaning of the produced nanotubes is easy.

The most effective catalysts for the CVD growth of CNTs are known to be metal nanoparticles like iron (Fe), cobalt (Co), and nickel (Ni). The peculiar ability [11] of these metals was suggested to relate to the catalytic activity or thermal decomposition of carbon precursors, the formation of meta-stable carbides, the diffusion of carbons, and the formation of graphitic sheets, etc.

2.2. Epoxy

Epoxy, also known as polyepoxide, is a thermosetting polymer formed from reaction of an epoxide "resin" with polyamine "hardener". Epoxy has a wide range of applications, including fiber-reinforced plastic materials and general purpose adhesives. Epoxy is a copolymer; that is, it is formed from two different chemicals. These are referred to as the "resin" or "compound" and the "hardener" or "activator". The resin consists of monomers or short chain polymers with an epoxide group at either end. Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A, though the latter may be replaced by similar chemicals. The hardener consists of polyamine monomers, for example triethylenetetramine (TETA). When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily cross linked, and is thus rigid and strong. The process of polymerization is called "curing", and can be controlled through temperature, choice of resin and hardener compounds, and the ratio of said compounds; the process can take minutes to hours. Some formulations benefit from heating during the cure period, whereas others simply require time and ambient temperatures.

2.2.1. Types and properties

There are two main categories of epoxy resins, namely the glycidyl epoxy, and non-glycidyl epoxy resins. The glycidyl epoxies are further classified as glycidyl-ether, glycidyl-ester and glycidyl-amine. The non-glycidyl epoxies are either aliphatic or cycloaliphatic epoxy resins. Glycidyl epoxies are prepared via a condensation reaction of appropriate dihydroxy compound, dibasic acid or a diamine and epichlorohydrin. While, non-glycidyl epoxies are formed by peroxidation of olefinic double bond. Glycidyl-ether epoxies such as, diglycidyl ether of bisphenol-A (DGEBA) and novolac epoxy resins are most commonly used epoxies.

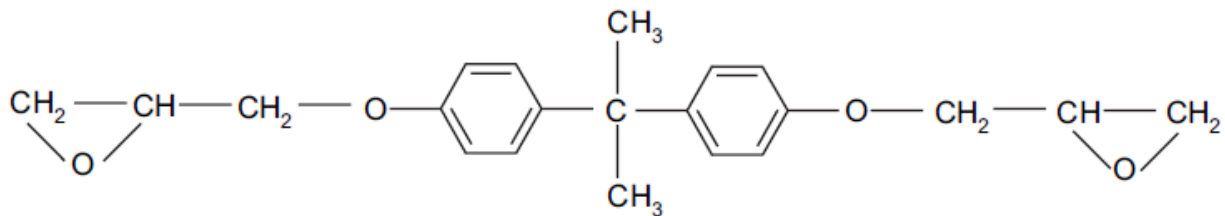


Figure 2.3. Structure of DGEBA [12]

Table 2.2. Properties of neat epoxy resin [13]

Property	Value
Tensile Strength	26 MPa
Young's Modulus	1.21 GPa
Elongation at break	2.33%
Storage modulus	1491 MPa
T _g	97.63 °C

2.2.2. Structural applications

Epoxy adhesives are a major part of the class of adhesives called "structural adhesives" or "engineering adhesives". These high-performance adhesives are used in the construction of aircraft, automobiles, bicycles, boats, golf clubs, skis, snowboards, and other applications where high strength bonds are required. In the aerospace industry, epoxy is used as a structural matrix material which is then reinforced by fiber. Typical fiber reinforcements include [glass](#), [carbon](#), [Kevlar](#), and [boron](#). Epoxies are also used as a structural [glue](#). Materials like [wood](#), and others that are 'low-tech' are glued with epoxy resin.

Epoxy based adhesive has gathered considerable attention in a variety of structural applications as a base material as well as a adhesive material due to its appreciable thermal and mechanical properties and economy. They are largely considered for enhanced thermal stability and glass transition temperature in combination with improved fracture toughness, better fatigue and fracture mechanism and higher wear resistance. The combination of all such properties can be made available only in composites material. In view of this an effort will be made in this work to produce carbon nanotube/nanofiber reinforced epoxy adhesive.

2.3. Dispersion of Carbon Nanotubes

Carbon nanotubes do not spontaneously disperse in polymers because of strong attractive interaction between the individual nanotubes (Figure 2.4) [13]. They aggregate to form bundles or ropes which are difficult to disrupt. Van der Waals forces are mainly responsible for aggregation. Various methods have been employed to break these clusters like use of solvents [14, 15, 16], surfactants [17, 18, 19, 20, 21], functionalization with fluorine [22], amine [23], ultrasonication, calendaring etc.

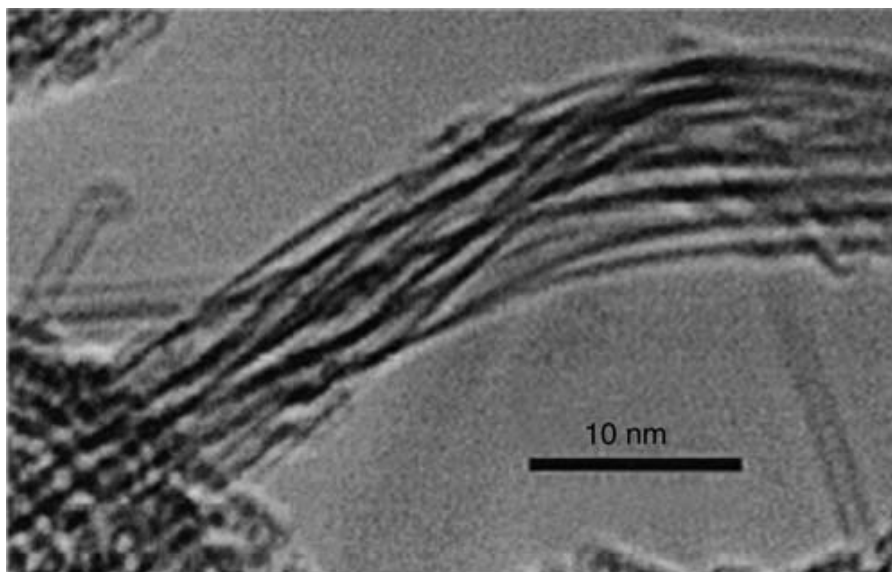


Figure 2.4. TEM image of partially exfoliated SWNT [14]

Ultrasonication is the irradiation of a liquid sample with ultrasonic (>20 kHz) waves resulting in agitation. Sound waves propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles or voids in the liquid, which then collapse violently (cavitation) during compression, creating very high local temperatures. These high temperatures reduced the viscosity and results in the deagglomeration.

A high-shear mixer disperses, or transports, one phase or ingredient (liquid, solid, gas) into a main continuous phase (liquid), with which it would normally be immiscible. A rotor or impellor, together with a stationary component known as a stator, or an array of rotors and stators, is used either in a tank containing the solution to be mixed, or in a pipe through which the solution passes, to create shear. A high-shear mixer can be used to create emulsions, suspensions, lyosols (gas dispersed in liquid), and granular products. It is used in the adhesives, chemical, cosmetic, food, pharmaceutical, and plastics industries for emulsification, homogenization, particle size reduction, and dispersion.

Liao *et al.* [24] made a comparative study of various dispersion techniques of SWNT reinforced epoxy. A tip sonicator was directly introduced in the solution of resin, solvent, and CNT. The samples were prepared according to the Table 2.3.

Table 2. 3. Processing parameters of nanocomposites [25]

Sample No.	Tip Sonication (hours)	Bath Sonication (hours)	Surfactant	Acetone
1	0	0	Y*	Y
2	6	6	0	0
3	6	0	0	Y
4	0	6	Y	0
5	6	0	Y	0
6	6	6	Y	Y

*Y = Yes, Used; 0 = Not used

DMA results are listed in the Table 2.4.

Table 2.4. DMA results of SWNT/SC-15 nanocomposites [25]

Sample No.	Storage Modulus	T _g (° C)	Storage Modulus increase (%)
1	1462	74.01	-1.90
2	1979	104.21	32.70
3	2249	75.38	50.84
4	1263	75.28	15.29

5	1667	84.23	11.80
6	1716	90.13	15.09
Neat Resin	1491	97.63	0

It can be seen that sample 3 has the highest mechanical properties. It used acetone as a solvent which improves the dispersion by having a diluting effect on the resin. Surfactant has a negative impact on the composite which can be seen through a reduced glass transition temperature. The solvents used in the dispersion process govern the properties of samples produced. Solvents having higher boiling points remain in the sample and have more affect on the samples. Acetone is found to be one of the best choice for solvents.

Functionalization of carbon nanotube is yet another method for dispersion and also improves interfacial bonding technique. Gojny *et al.* [25,26] used amino-functionalized MWCNT reinforced epoxy and tested thermo-mechanically. TEM confirmed better dispersion due to functionalization. The glass transition temperature increased linearly with increased fiber content. Kim *et al.* [27] demonstrated that plasma-functionalized CNT gave best properties followed by amine treated CNT and acid treated CNT.

2.4. Mechanical Properties

Mechanical properties of a CNT reinforced epoxy composites are determined by several factors. Catalyst systems used in the production of carbon nanotubes have a heavy influence on the mechanical properties of CNT/Epoxy composites. Two types of catalyst systems were observed and their influence on mechanical properties were studied by Breton *et al.* [28] - $\text{Co}_x\text{Mg}_{(1-x)}\text{O}$ solid solution (Type 1) or on a Co/NaY supported catalyst (Type 2) at 600°C. Type 1 MWNTs were found to be difficult to disperse and impregnate with epoxy resin and hence its applications in composites wasn't suited. This difference mainly occurs due to a high specific surface area of 220m²/g and mesoporous volume of 1.0 cm³/g which gives rise to more entanglements between the nanotubes. In comparison to type 1 MWNTs, the specific surface and the mesoporous volume for the Type 2 MWNTs are only 130m²/g and 0.5 cm³/g, respectively.

Types of carbon nanotubes and their functionalization is another factor. Surface area and the specific

mechanical properties of the nanofillers and the aspect ratio are the determinant factors for the mechanical reinforcement by these nanoparticles. The influence of different types of carbon nanotubes and their functionalization on the mechanical properties was investigated . It was found [^{29,30}] that DWCNT–NH₂ reinforced epoxy shows the largest improvement of strength and stiffness under the given processing conditions. Amino groups present on the CNT surface will react with epoxy and form covalent bonds resulting in a significantly enhanced interfacial adhesion. SWNTs have even more potential to improve the mechanical properties of the matrix because their high surface area provides an excellent dispersion and it results in a strong interface.

Liu *et al.* [³¹] observed the effect of matrix hardness on the mechanical properties of the nanocomposites . Two types of hardener were used, so two types of matrices were attained; one was glassy and the second was rubbery (both at room temperature). The MWNTs were functionalized with carboxylic groups through treatment with a 1:3 volume concentrated solution of HNO₃/H₂SO₄ in a sonicator. Due to lower viscosity, the nanotube dispersion was found to be much better in the rubbery epoxy resin than the glassy epoxy. This was indicated by their modulus values. For the rubbery epoxy composites Young's modulus went up by 28% as compared to unreinforced matrix using 1 wt.% functionalized nanotubes whereas no improvement in modulus was shown in case of glassy epoxy, but a significant 50% improvement in impact toughness was observed, compared to the unreinforced matrix. Observations were also made by preparing resins of different stiffness by varying the amount of hardener [³²] used in the curing reaction and also the curing time. A small proportion of hardener and lesser curing time resulted in ductile matrices.

Allaoui *et al.* reported the tensile behavior of a MWNT reinforced rubbery epoxy resin cured using an over-aged hardener [³³]. This made it possible to know the effect of nanotubes addition on the whole stress–strain curve which is shown in figure 2.5. The Young's modulus and the yield strength of the composite are doubled by adding 1 wt. % of CNT and quadrupled with 4 wt.% CNT.

The fatigue behavior of single-walled carbon nanotube reinforced epoxy composites was reported by Ren *et al.* [³⁴] . Behavior of the composites under repeated mechanical loads is necessary to predict their long term performance. Unidirectionally aligned SWNT ropes synthesized by the hydrogen/argon electric arc discharge method were used to reinforce the epoxy resin. Higher values of cyclic stresses were obtained in the case of SWNT composites compared to carbon fibers and hence SWNTs reinforced composites were expected to give better long term performance.

Stiffness and damping properties of CNT reinforced epoxy composites are of importance for use in

structural vibration applications [35]. It was observed that multiwalled nanotubes were more effective than single walled carbon nanotubes in enhancing the damping characteristics of the nanocomposites. Fundamental damping ratio increased up to 700% compared to plain epoxy resin beam.

The curing cycle has a strong influence on the mechanical properties of carbon nanotubes reinforced epoxy composites. An increment in the properties of resin and also nanocomposites can be observed as curing time and the temperature increases [36]. Improvement in the flexural properties has also been found in the CNT reinforced epoxy composites as a result of a very good dispersion of the nanotubes in the epoxy matrix and also a very good inter phase between carbon nanotubes and epoxy resin [37].

Table 2.5. Mechanical properties of nanoparticle reinforced composites [30]

Resin/Filler type	Wt content (%)	Young's modulus (MPa)	Ultimate Tensile Strength (MPa)	Fracture Toughness K_{IC} (MPa m^{1/2})
Epoxy	0.0	2599	63.8	0.65
Epoxy/SWCNT	0.05	2681	65.84	0.72
Epoxy/MWCNT	0.1	2780	62.97	0.79

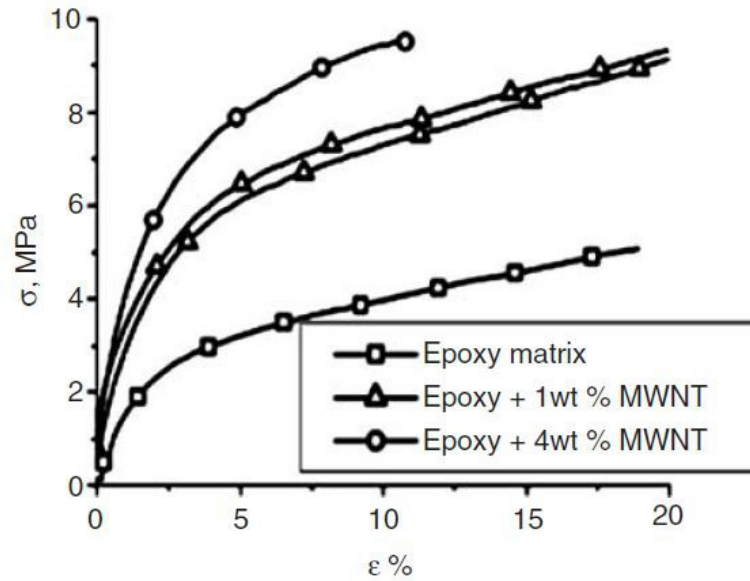


Figure 2.5. Tensile test stress-strain curve of the resin and its composites [34]

2.5. Thermal Properties

The factors influencing the thermal conductivity of carbon nanotube reinforced composites are the overall size of the interface, the aspect ratio of the nanotubes and the interfacial adhesion between the nanotubes and the matrix. The huge interface as a result of nanometric size leads to strong phonon-scattering at the interface and thus reduces conduction of photons. So a relatively low interfacial area, weak interfacial adhesion and the existence of shielded internal layers are necessary to facilitate conduction of phonons and minimize coupling losses. Because of the larger diameter, MWCNTs are the most effective among the carbon nanotubes to improve the thermal conductivity of epoxies [38].

Also the phonon vibrations in the SWNTs can be dampened by the matrix interaction, while in the MWNTs the phonons can be carried in the inner walls without hindrance [39] but as a whole because of the nanodimension, carbon nanotubes are not suitable for an enhancement of the thermal conductivity of polymer-based composites.

Bryning *et al.* [40] reported that the thermal conductivity measurements of purified singlewall carbon nanotube (SWNT) epoxy composites. Thermal conductivity of two types of composites prepared using suspensions of SWNTs in N-N-Dimethylformamide (DMF) and surfactant stabilized aqueous SWNT suspensions was investigated and it was found that DMF-processed samples, where higher nanotube loadings are difficult to obtain, exhibit a modest enhancement in the range Φ (carbon nanotube weight fraction) 0.001 to 0.005. At $\Phi = 0.005$, the enhancement is about $(27\pm 5)\%$ over pure epoxy, whereas surfactant processed samples, which permit greater SWNT loading, exhibit no measurable enhancement of thermal conductivity below $\Phi = 0.01$ and larger overall enhancement of $(64\pm 9)\%$ at Φ around 0.1. The difference in the enhancement of thermal conductivity with nanotube loadings of the two types of suspensions is due to a ten-fold larger SWNT/solidcomposite interfacial thermal resistance in the surfactant-processed composites compared to DMF-processed composites.

2.6. Thermo-mechanical Properties

Functionalization of MWCNTs influences the glass transition temperature of the nanocomposites based on epoxy. In a study by Gojny *et al.* [41] they investigated the thermo-mechanical behavior of the nanocomposites based on epoxy reinforced with different loadings of functionalized and non-functionalized carbon nanotubes. Dynamic Mechanical Analysis was done and a dependence of the nanotube content on the glass transition temperature (T_g) was observed.

An increase in the amount of filler led to an increase of T_g , and amino functionalized nanotubes sample showed a stronger influence on T_g in comparison to composites containing non-functionalized nanotubes (Figure 2.6). This is because functionalization of carbon nanotubes has a strong influence on the interfacial interaction between the epoxy matrix and CNT.

Miyagawa *et al.* reported [42] that the synthesis, and thermo physical properties of nanocomposites prepared using biobased epoxy reinforced with fluorinated single-wall carbon nanotubes. The biobased epoxy containing diglycidyl ether of bisphenol F (DGEBA) and epoxidized linseed oil (ELO) was cured with an anhydride curing agent. Sonication was the technique used to disperse the nanotubes in the epoxy matrix. The storage modulus of the epoxies at 30°C increased by around 0.66–0.83 GPa with the addition of only 0.20wt% (0.16 vol.%) of fluorinated SWCNT (FSWCNT), as shown in Figure 2.7,

representing an approximate 25% improvement.

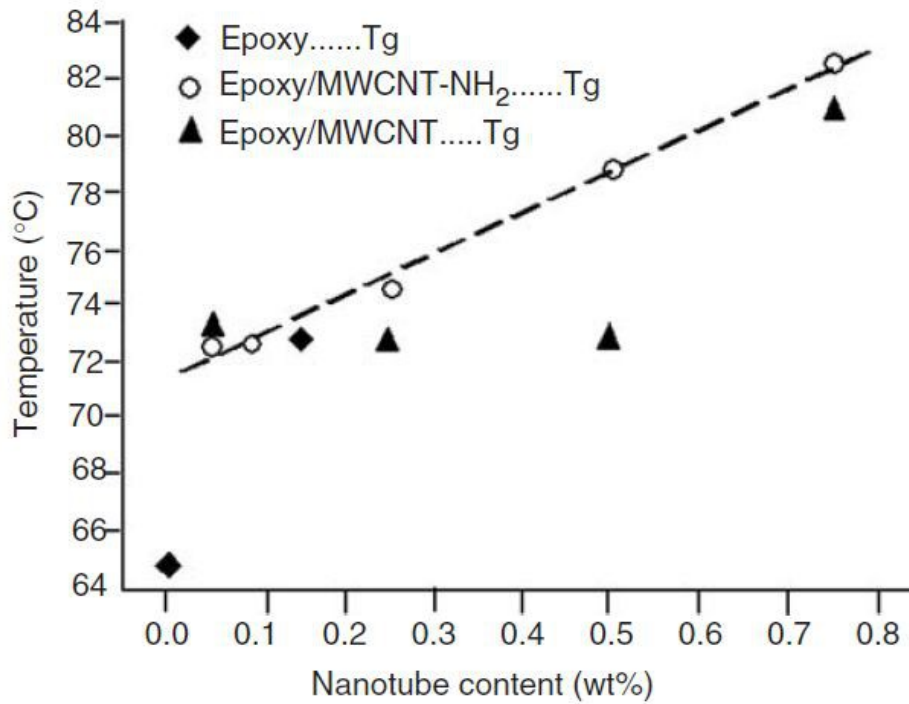


Figure 2.6. Glass transition temperature as a function of nanotube content [42]

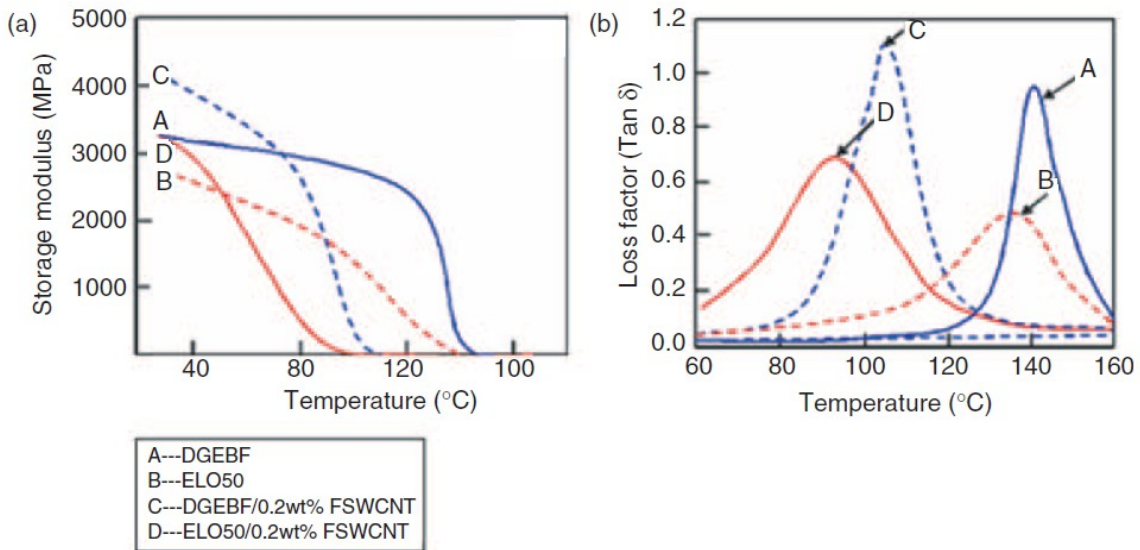


Figure 2.7. DMA measurements for anhydride-cured epoxy/FSWCNT nanocomposites [43]

This suggests that individual FSWCNTs were well separated because of the fluorination of the SWCNT and thus they were homogeneously dispersed in the epoxy matrix. The stoichiometry of epoxy matrix was found to have a significant influence on the thermal behaviour of the nanocomposites. The glass transition temperature was maximized only when stoichiometry was achieved in the epoxy matrix. An improvement of the storage modulus in SWCNT/epoxy nanocomposites with increasing loading of nanotubes has also been observed [43].

SWNT reinforced epoxy composites was fabricated [44] with a storage modulus as high as 15 GPa using a novel technique. They have used the bucky paper/resin infiltration approach in which SWNTs were first dispersed in water-based suspension with the aid of surfactant and sonication and then, through a filtration process, SWNTs were fabricated into thin membranes called buckypapers to form networks of SWNT ropes. The nanotube/resin impregnation of the produced buckypaper was then performed by infiltrating acetone diluted epoxy resin/hardener mixture along the thickness direction of the bucky paper for several hours. Curing was done in a hot press to produce nanocomposites of multiple layer buckypapers with a nanotube loading as high as up to 39 wt%.

2.7. Summary and Problem Statement

Reinforcing epoxy matrix with carbon nanotubes in the form of two phase composites has been widely researched and found helpful in improving several properties such as mechanical, thermo-mechanical, thermal, electrical etc., but the ability to transfer these properties of carbon nanotubes in composites lies in the uniform dispersion of carbon nanotubes in the resin which is to be ensured. With respect to mechanical properties strong interface is another important criterion which is necessary to transfer the forces from matrix to the nanotubes. Functionalization of carbon nanotubes by different techniques helps to achieve strong nanotube-matrix interface.

In contrast to various purification techniques used to obtain maximum CNT yield after its production very little work has been reported on the usage of CNTs in making the composite readily after its production. Our work would be regarding the comparison of mechanical and thermo-mechanical properties of epoxy nanocomposites prepared using readily obtained CNTs and purified CNTs prepared

using Cobalt catalytic chemical vapor deposition method. For dispersing the nanotubes into the epoxy matrix an innovative technique called Ultrasonic Dual Mode Mixing (UDMM) will be used. A flowchart of the methodology to be followed for the planned studies is shown in Figure 2.8.

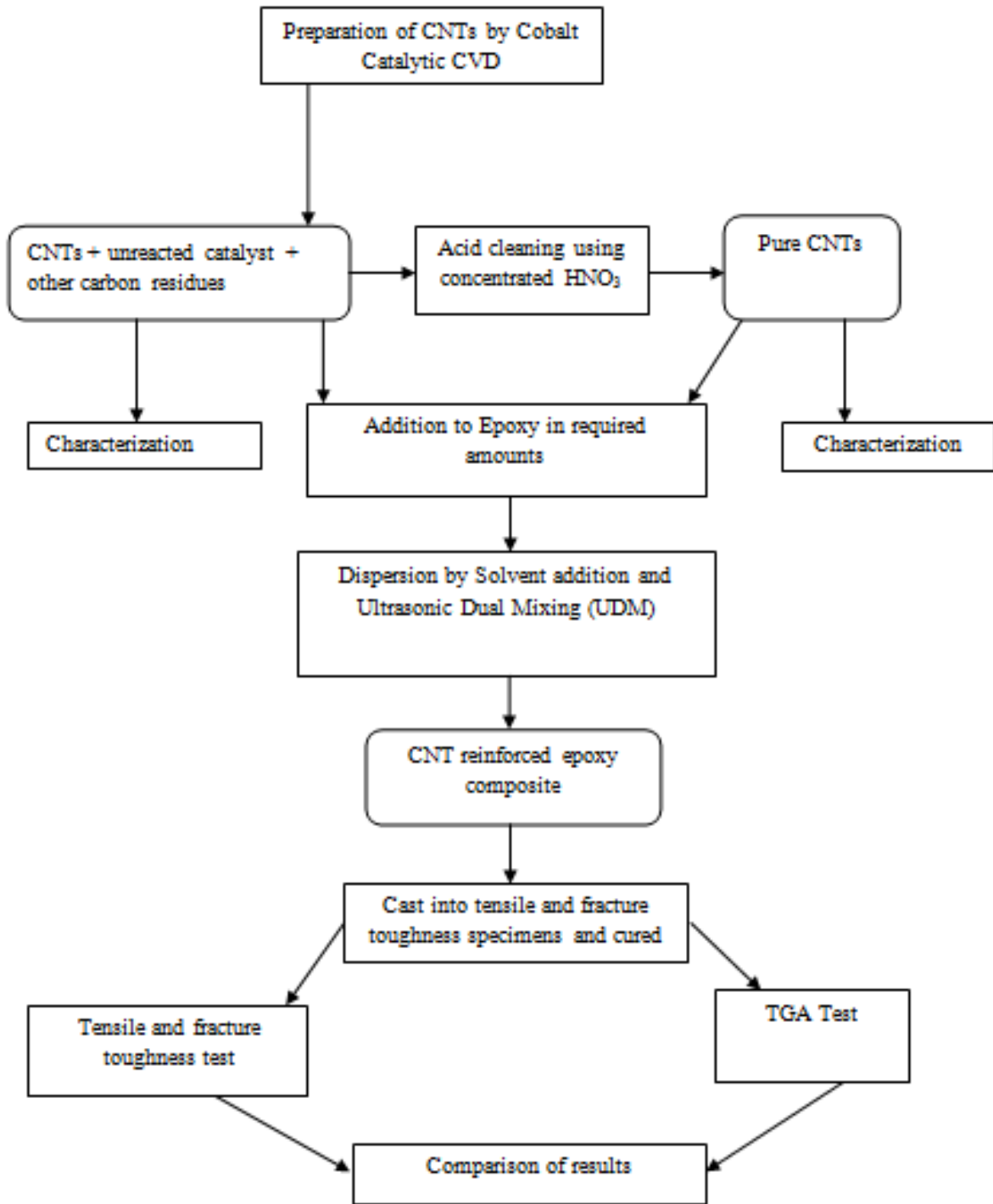


Figure 2.8. Flowchart of proposed studies

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. Objective

1. To synthesize Carbon Nanotubes (CNTs) by Chemical vapour deposition (CVD) technique and their characterization using FESEM/TEM.
2. To incorporate CNTs in epoxy adhesive via ultrasonic dual mixing process.
3. To study thermal properties of CNTs reinforced epoxy composite by DTA/TGA/DTG analysis
4. To study mechanical properties of CNTs reinforced epoxy composite by tensile testing and tensile fracture surface analysis.

3.2. Chemicals used

Cobalt (II) acetate tetrahydrate, Citric acid monohydrate, Nitric acid, Acetone, Ethyl methyl ketone, Ethanol, Silicon oil, Distilled water, Ammonia gas, Acetylene gas, Epoxy adhesive (Araldite AW106) and Hardener HV 953U.

3.3. Experimental setup

Chemical vapour deposition (CVD) furnace, Refractory furnace, Oven, Ultrasonic dual mixer setup, Magnetic Stirrer, Vacuum pump and glass desiccators.

3.4. Procedure followed:-

3.4.1. Synthesis of CNTs reinforced epoxy composites:-

Ultrasonic dual mode mixing (UDMM) via ultrasonic vibration along with magnetic stirring was employed to prepare CNTs reinforced epoxy composite. Master batch slurry of epoxy resin containing 2 wt% of CNTs was prepared. The master batch slurry was dissolved in a suitable proportion of 1:4 of epoxy resin to methyl ethyl ketone (MEK) to lower its viscosity to the desired level. The UDMM process was employed at optimized process parameters given below:- (reported in PhD thesis of Sudipta, MMED, IITR).

The maximum power output is 500 watts and is applied at a frequency of 20 kHz using a 13 mm diameter

stainless steel horn. The mixing parameters were as follows:-

Solvent used: Methyl Ethyl Ketone
Time: 4 hrs

Amplitude: 60 %

Frequency: 20 KHz

Digital pulse:-
10 sec –ON
20 sec – OFF

Energy: 340 Joule/cycle
Power: 34 Watt/cycle

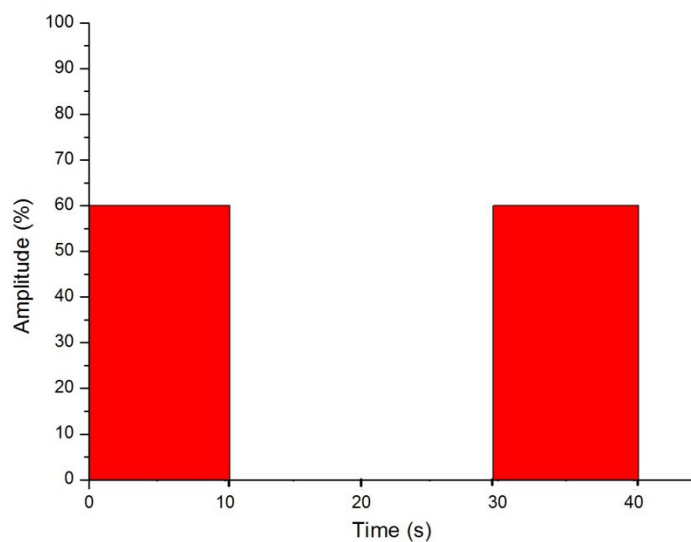


Figure 3.1. Process cycle of Ultrasonic Dual Mode Mixing



Figure 3.2. Setup of Ultrasonic Dual Mode Mixing Process (magnetic stirrer along with ultrasonic processor)

During the UDMM, temperature of the slurry was maintained at 25 to 30 °C in an iced water bath. After completion of UDMM process, the MEK was removed from the slurry by placing it into an oven at 75 °C under vacuum of 1.5×10^{-3} torr for 2 hours. The removal of MEK was confirmed by comparing the weight of glass beakers containing the resin with or without CNTs before addition and after removal of MEK to an accuracy of 0.1 mg. Further, fresh epoxy resin was added to the master batch slurry to set the desired composition of CNTs of 0.5%, 1% and 2% in the epoxy resin. Hardener was added in a stoichiometric ratio (100% by vol. or 80% by weight as specified by Araldite user manual) to the slurry. The mixing was followed by glass rod stirring for 10 min and degassing at room temperature for the removal of air entrapped during mixing. The resulting CNTs reinforced epoxy composites were then poured in transparent Perspex sheet tensile moulds and also on glass Petri-dishes coated with a thin layer of paraffin wax, and placed in hot air oven for 16 h at 40 °C for curing. The oil coating was removed from specimens using acetone. The cured tensile specimens were polished with a fine grade emery paper to obtain samples of uniform thickness and specimens removed from Petri-dishes were cut down to small pieces

for thermal analysis. The above mentioned process was followed for both the untreated and acid treated CNTs.

3.5. Characterization by FESEM / EDAX

FESEM ([Field Emission Scanning Electron Microscopy](#)) and EDAX (Energy Dispersive X-ray Analysis) were employed for the analysis of untreated and acid treated CNTs and CNT reinforced composites has been performed. It was done to analyse the carbon nanoforms produced and to have a rough estimate of the amount of unreacted catalyst left from the CVD process. Fracture surface analysis of tensile test specimens was also studied by FESEM.

3.6. Mechanical Property testing

Both tensile and fracture toughness tests were conducted using the Universal Testing machine of Department of Metallurgical and Materials Engineering, IIT Roorkee.

3.6.1. Tensile test

Tensile specimens of nanocomposite adhesives are made according to the ASTM standard D 638-03.

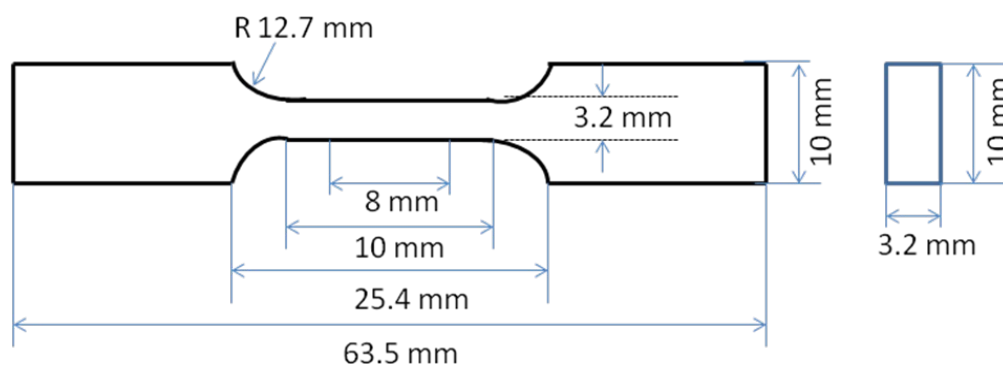


Figure 3.3. Prepared tensile specimen

3.6.2. Fracture toughness test

Fracture toughness specimens of nanocomposite adhesives are made according to the ASTM standard 5045.

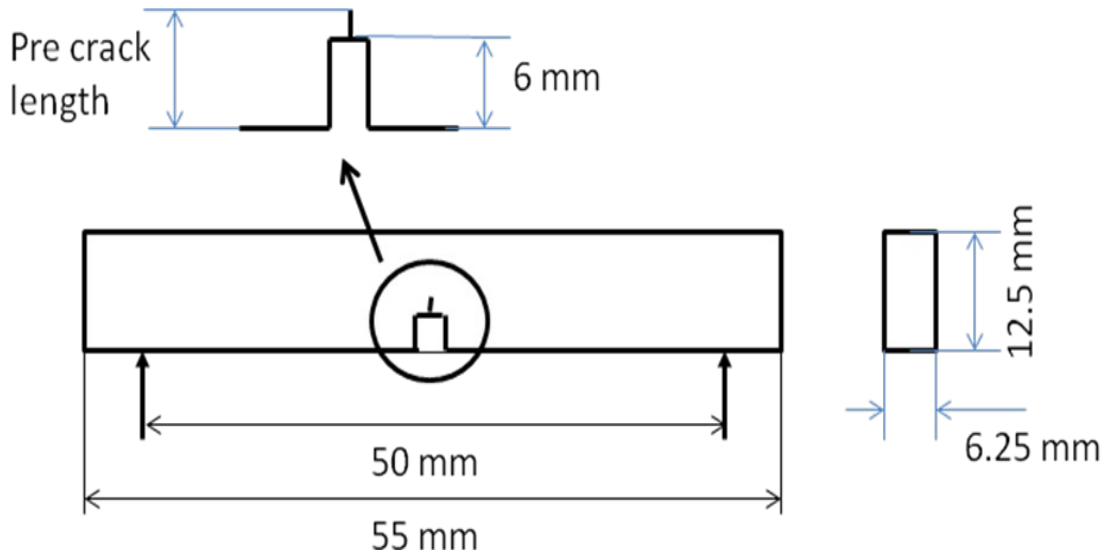


Figure 3.4. Fracture toughness test specimen

3.7. Thermal property testing

Differential Thermal analysis (DTA) was done to determine the glass transition temperature, decomposition temperature and Integral Procedural Decomposition Temperature (IPDT) of the epoxy. The thin layer of sample prepared for thermal analysis was cut into very small pieces to do the DTA. The DTA were carried out by thermal analyzer at Institute Instrumentation Centre (IIC), IIT Roorkee. (Perkin– Elmer, Pyris Diamond) using alumina as the reference material. Process parameters are given below:-

Atmosphere: N₂ gas
Temp. range: Room temp(25 °C) – 700 °C

Flow rate: 200ml/min
Heating rates: 5,10,15⁰ C/min

CHAPTER 4

RESULTS AND DISCUSSIONS

Untreated and acid-treated CVD output will be referred to as “unclean” and “clean” CNTs and their respective composites as unclean CNT/epoxy nanocomposite (CEN) and clean CENs hereafter in the report.

All experiments were carried out as mentioned in the third chapter of the report. Due to unavailability of vacuum degassing equipment during the later stages of the project clean CNT loading to prepare tensile and fracture toughness samples could not be done. Since the thermal properties are affected by bubbles in the specimen these tests could be carried out anyway. Unclean CNT-epoxy composite itself showed

improvement in mechanical properties which is reported in section 4.2.

4.1. Microscopic characterization (FESEM and EDAX)

FESEM and EDAX analysis was done to investigate the presence of CNTs from the CVD output. The catalyst was analysed to check its effect of size and size distribution on the carbon nanoforms produced. Further analysis of fracture surface was done to reveal the effect on addition of filler to epoxy which generally shows a smooth fracture surface.

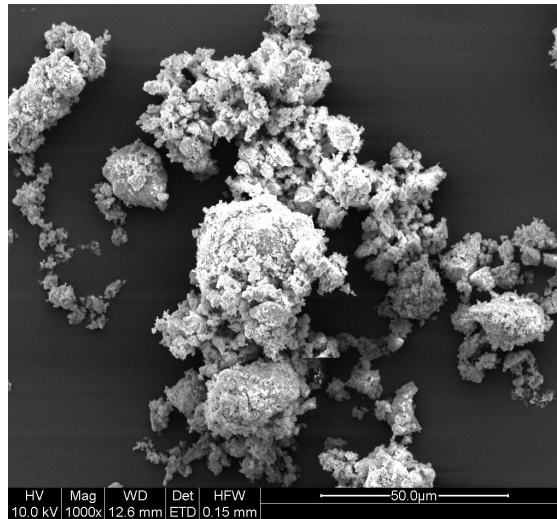
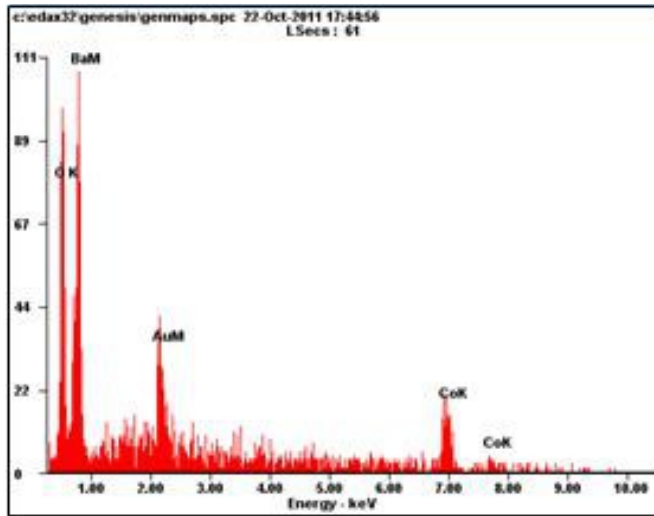


Figure 4.1. FESEM image of catalyst for CNT preparation

The above image gives a sense of the size and size distribution of the catalyst (Cobalt oxide) prepared by the sol gel technique. It is on these parameters that the type of carbon nanoform produced is dependent on. Here we see huge clusters of the catalyst particles. This is not advisable if we are to achieve a high yield of MWCNTs from the CVD output.



<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>OK</i>	08.25	27.21
<i>AuM</i>	14.83	03.97
<i>CoK</i>	76.91	68.82
<i>Matrix</i>	Correction	ZAF

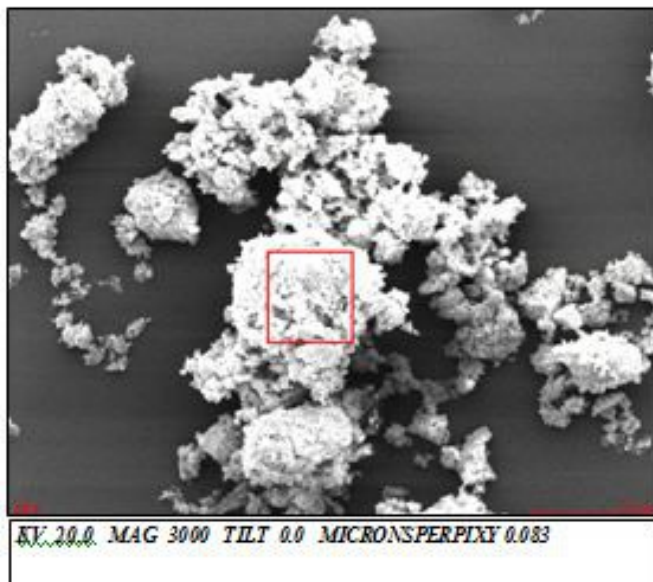


Figure 4.2. EDAX analysis of the catalyst

As we expected the EDAX analysis shows presence of Cobalt and Oxygen. Cobalt oxide nanoparticles act as the catalyst for the chemical vapor deposition process for producing carbon nanoforms.

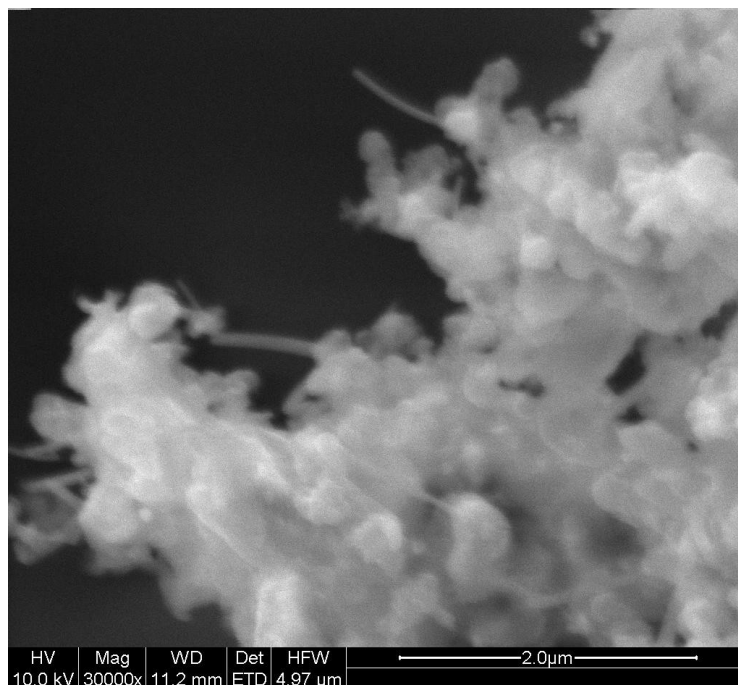
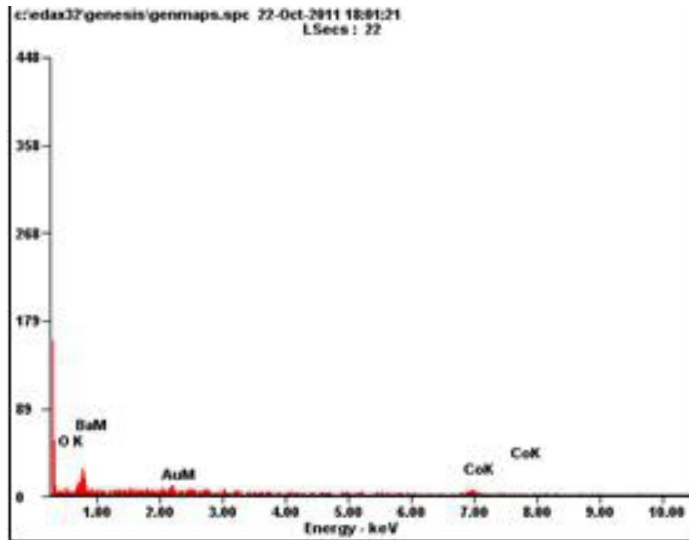


Figure 4.3. FESEM image showing Carbon nanotubes

This batch of unclean carbon nanofoms shows the presence of carbon nanotubes. The region surrounding the CNTs were believed to be a mixture of unreacted catalyst and other amorphous forms of carbon. To investigate this an EDAX analysis of the same was done.



<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	75.47	93.78
<i>OK</i>	00.60	00.56
<i>AuM</i>	02.28	00.17
<i>CoK</i>	21.65	05.48
<i>Matrix</i>	Correction	ZAF

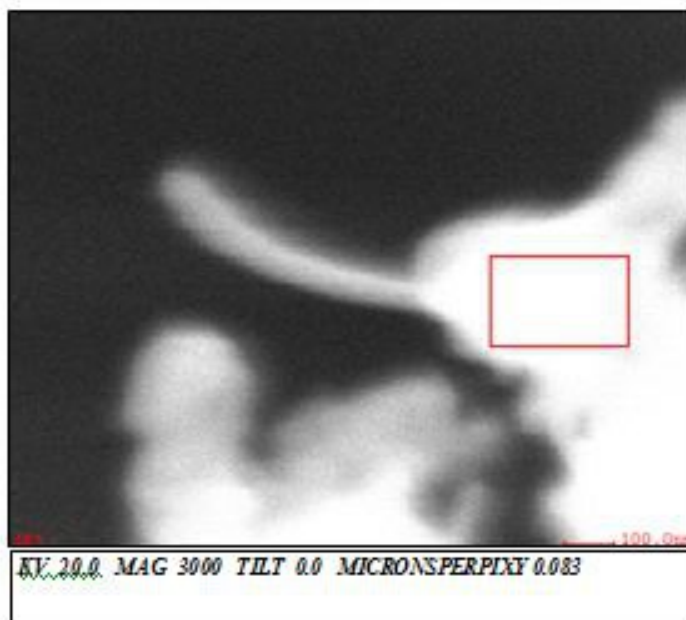
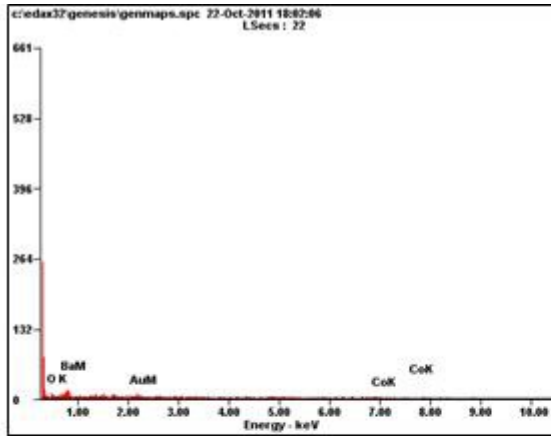


Figure 4.4. EDAX analysis of the region around carbon nanotubes

An EDAX analysis of region around the supposed carbon nanotubes revealed a slight presence of cobalt. Since this batch wasn't acid cleaned there is the presence of unreacted catalyst from the CVD furnace. Cobalt oxide inside the furnace is reduced to cobalt by ammonia. Literature has shown presence of cobalt

nanowires inside the nanotubes.



Element	Wt%	At%
CK	95.56	98.90
OK	01.15	00.89
AuM	03.29	00.21
CoK	00.00	00.00
Matrix	Correction	ZAF



Figure 4.5. EDAX elemental analysis of the CNT tip

Analysis of the tip of the supposed carbon nanotubes confirmed our assumptions since it is almost pure carbon.

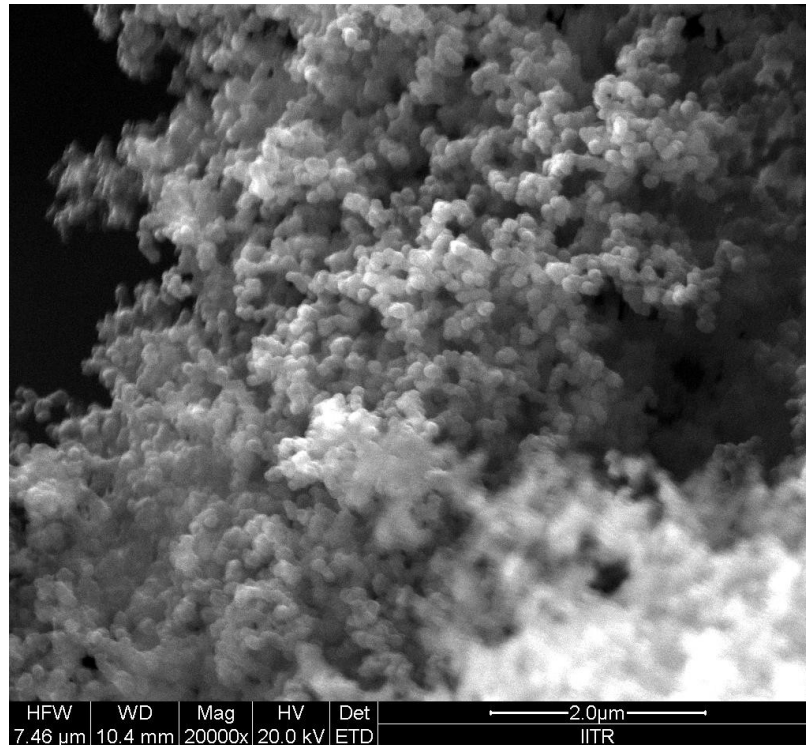


Figure 4.6. FESEM image of a certain batch of clean carbon nanoforms samples showing a high amount of nanobeads

This certain batch of cleaned nanoforms reveal a significant amount of nanobeads formation. This happens when the acetylene flow rate in the CVD furnace is higher, ie. the higher the acetylene flow rate higher amount of carbon nanobeads are formed. Nanobeads aren't known to possess the mechanical properties of CNTs. So ultimately almost all the improvement in the properties of the nanocomposite can be attributed to the amount of CNTs present in the batch of carbon nanoforms produced.

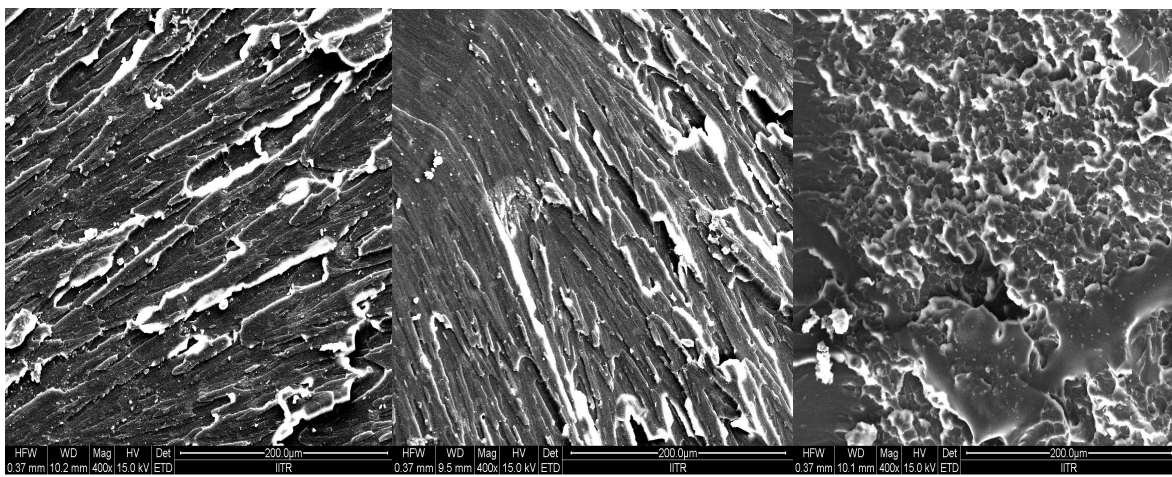
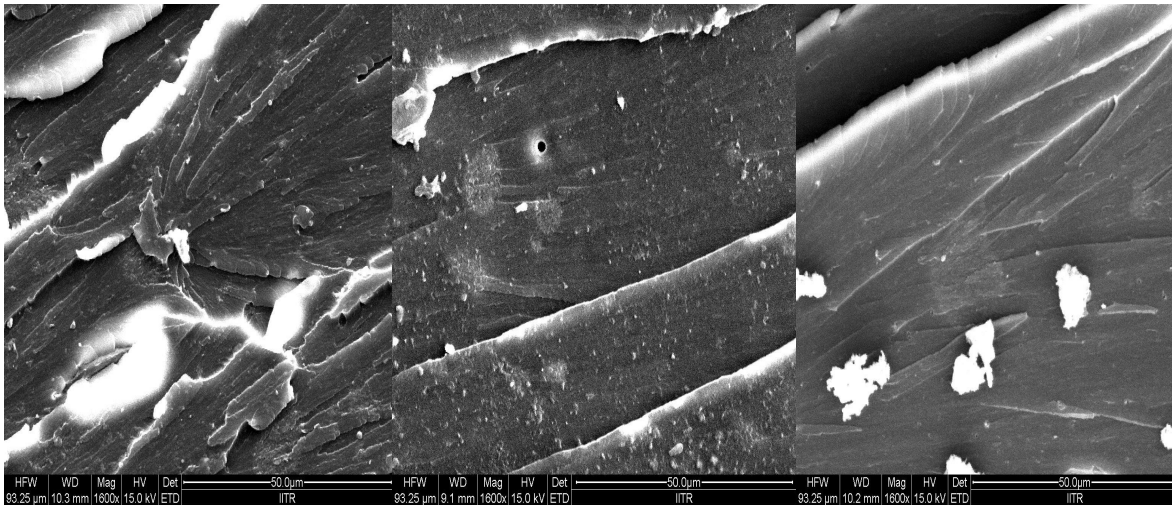


Figure 4.7. FESEM image of fracture surface of 0.5,1 and 2 wt% (from left to right) unclean CNT/epoxy nanocomposites respectively at two different magnifications (1600x - top and 400x – bottom)

As expected from the literature, rough fracture surfaces are seen. As evident from the third picture in the top, clusters are not completely broken in this case. This is the 2 wt% CEN, having the maximum amount of filler loading. In this case, the ultrasonic dual mode mixing wasn't efficient enough to break clusters in this case.

4.2. Mechanical properties

4.2.1. Tensile strength

Samples loaded showed a slight amount of necking before fracture. The brittle nature of epoxy was decreased to a certain extent by CNT addition.

Table 4.1. Tensile strength values of unclean CNT/epoxy nanocomposite with their composition

Filler wt%	T1(MPa)	T2(MPa)	T3(MPa)	T4(MPa)	Tensile stress avg. (MPa)
Neat epoxy (0%)	-	-	-	-	40.05**
0.5 wt%	40.85	41.45	41.53*	40.42	40.90
1 wt%	38.78	42.59	41.31	--	40.89
2 wt%	47.04	40.75	37.64*	42.3	43.36

*discarded values because of sample irregularity

**previous work of PhD scholar

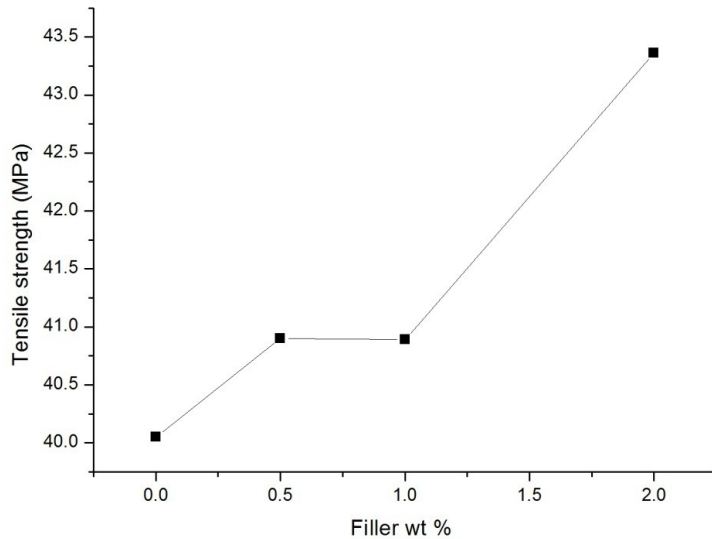


Figure 4.8. Plot of tensile strength vs. filler wt% for unclean CNT/epoxy nanocomposites

Since the mechanical properties rely on good interfacial adhesion for improvement it is clear that the interface has adhered but not as effective since there is lesser amount of CNTs in the filler. Hence it shows very less improvement in tensile strength. The values for 0.5 and 1 wt% are nearly the same, but it goes up for 2 wt%. Larger agglomerates in the case of 2 wt% are a probable cause for this.

4.2.2. Elastic modulus

It defines the tendency of a material to define elastically. Thermosetting polymers like epoxy have shown a range of elastic modulus values, from a few hundred MPas to around 20 GPa. One of the general purposes of filler addition to epoxy is to increase its value.

Table 4.2. Elastic modulus values of unclean CNT/epoxy nanocomposite with their composition

Filler wt%	E1(MPa)	E2(MPa)	E3(MPa)	E4(MPa)	Elastic modulus avg. (MPa)
Neat epoxy (0%)	-	-	-	-	511**

0.5 wt%	582	615	597*	609	602
1 wt%	587	640	620	--	615.67
2 wt%	675	602	657*	661	646

*discarded values because of sample irregularity

**previous work of PhD scholar

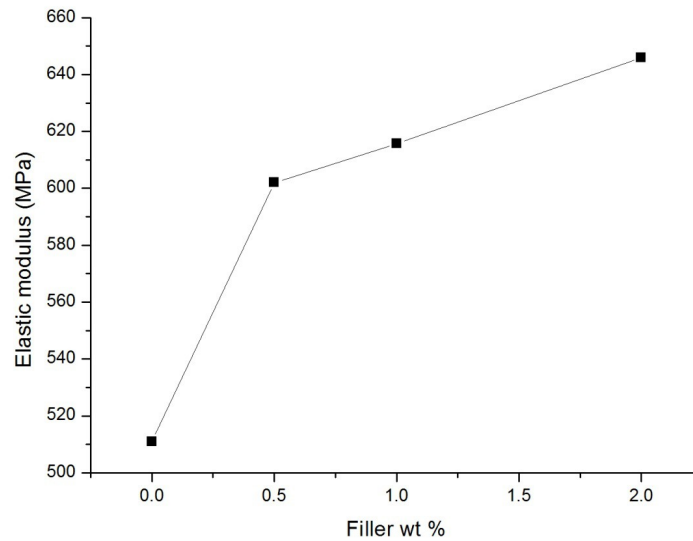


Figure 4.9. Plot of elastic modulus vs. filler wt% for unclean CNT/epoxy nanocomposites

Elastic modulus has shown an almost perfect linear increase with filler load, reaching the maximum value at 2 wt%. This result may be explained by the fact that the agglomerates in the untreated MWNT composites act as large particles and thus provide higher apparent filler loading.

4.2.3. Fracture toughness and energy

Table 4.3. Variation of fracture toughness and strain energy of different CEN compositions

Filler wt%	Average K_{IC} ($MPa \cdot m^{1/2}$)	Average G_{IC} (J/m^2)
Neat epoxy (0%)	0.695	51.145

0.5	1.3626	112.027
1	1.8342	165.7718
2	1.0027	82.8285

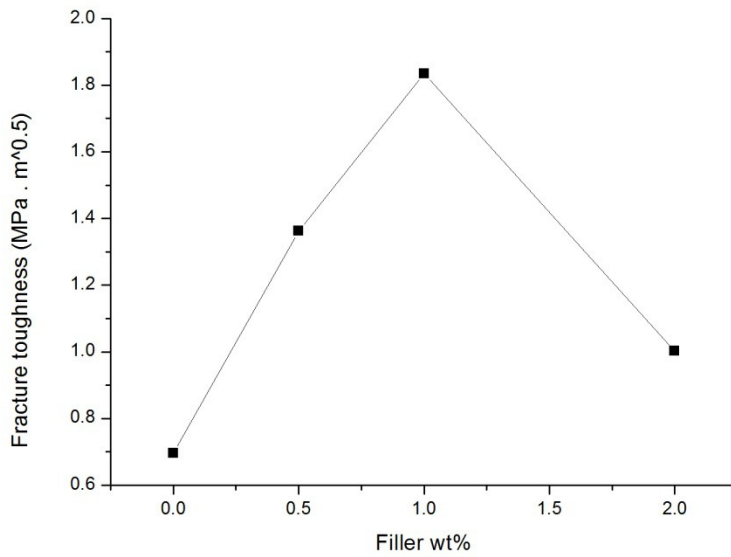


Figure 4.10. Plot of Fracture toughness against filler (unclean CNTs) wt%

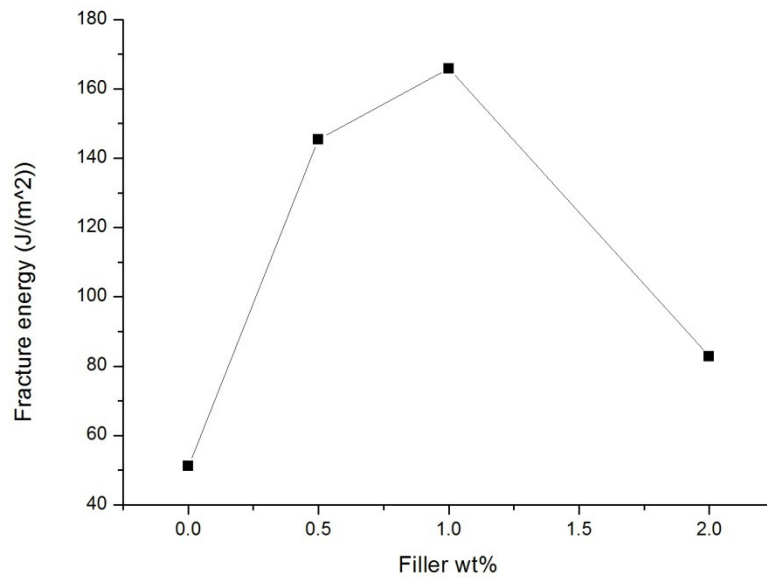


Figure 4.11. Plot of Fracture energy vs. filler (unclean CNT) wt%

Both fracture toughness and energy values reaches a maximum at a loading of 1 wt% and then dips substantially for 2 wt%. This is because there is a possibility of a suppressing of interfacial failure which adversely affects the toughness.

4.3. Thermal properties

4.3.1. Glass transition temperature (T_g)

The glass-liquid transition (or glass transition for short) is the reversible transition in [amorphous](#) materials (or in amorphous regions within [semicrystalline](#) materials) from a hard and relatively brittle state into a molten or [rubber](#)-like state. DTA results consists of three thermograms and the DTA vs. Temperature one is used to calculate T_g . The figure shown below shows the calculations in the case of a 0.5 wt% clean CEN.

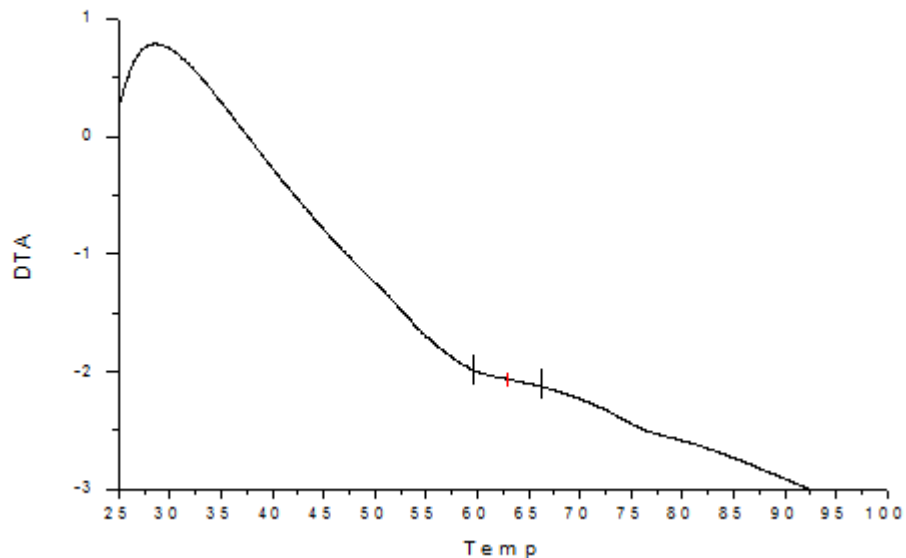


Figure 4.12. Plot showing T_g calculation of a 0.5 wt% clean CNT/epoxy nanocomposite

Table 4.4. Average values of T_g of both unclean and clean CNT/epoxy nanocomposites

Filler type and wt %	Glass transition temperature T_g (°C)
Neat epoxy (0%)	54.48
Unclean	
0.5 %	59.313
1 %	59.49
2 %	57.49
Clean	
0.5 %	65.59
1 %	66.6
2 %	67.96

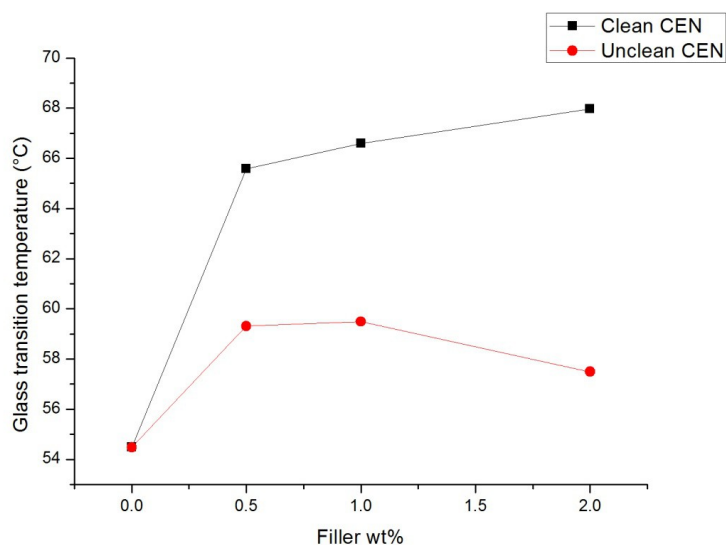


Figure 4.13. Plot showing variation of glass transition temperature against both unclean and clean CEN

For clean CEN there is almost a linear increase in the value of T_g with the filler loading. For the unclean CEN there is a very slight increase till 1 wt% and then a drop to the 2wt% nanocomposite.

4.3.2. Thermal Stability

Thermal stability is the stability of a [molecule](#) at high [temperatures](#); i.e. a molecule with more stability has more resistance to decomposition at high temperatures. In our case, the TG thermograms from DTA tests show a measure of decomposition of the material. Different weight % decomposition temperatures were noted and compared.

Table 4.5. Values of different decomposition temperatures against their respective nanocomposite samples

Filler type and wt%	5 wt% decomp. T (°C)	10 wt% decomp. T (°C)	Onset T (°C)	Offset T (°C)
Neat epoxy (0%)	235.36	310.20	311.19	450.11
Unclean				
0.5 %	285.04	335.21	337.20	479.71
1 %	288.34	337.48	338.26	480.52
2 %	283.71	335.62	336.57	480.53
Clean				
0.5 %	273.94	332.6466667	325.56	480.92
1 %	285.5947667	335.6210067	330.84992	482.9033
2 %	293.59	345.85	331.53	493.33

Onset and onffset temperatures signify the temperatures at which decomposition rates begins a marked step increase and at which it subsides respectively. All the above values are obtained from the TG curve.

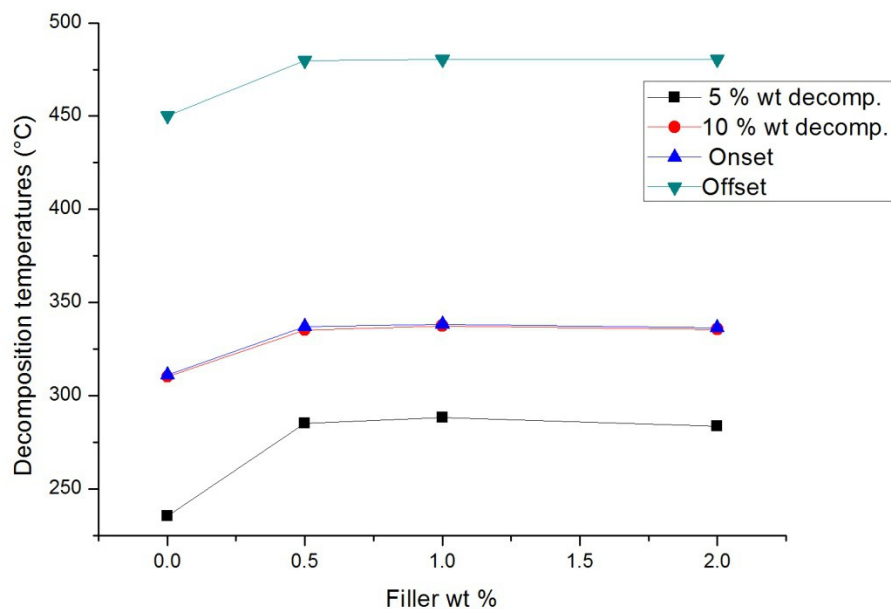


Figure 4.14. Plot of different Decomposition temperatures vs. filler wt% of unclean CEN

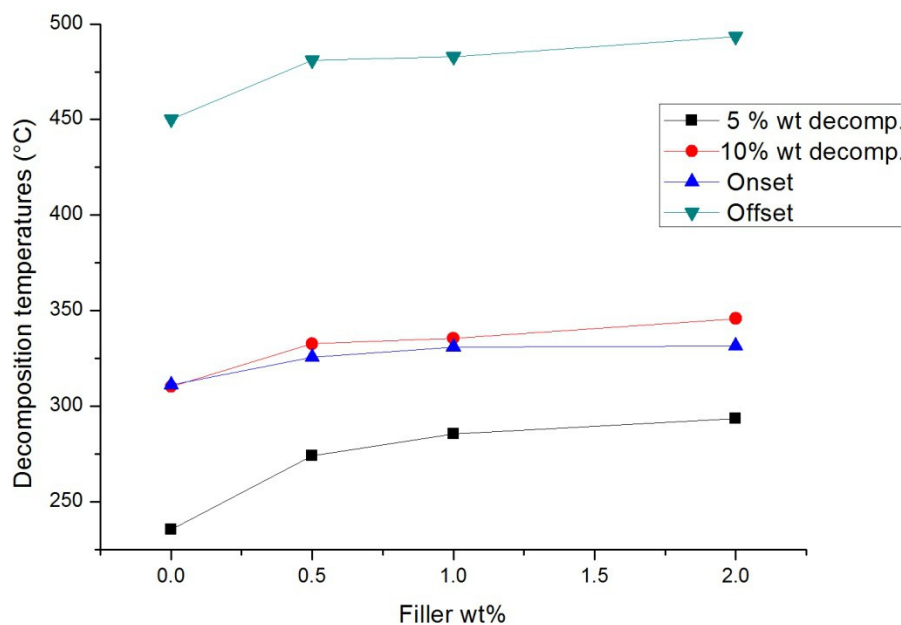


Figure 4.15. Plot of different Decomposition temperatures vs. filler wt% of clean CEN

Almost all percentage weight loss and onset and offset decomposition temperatures are showing an increasing trend with the filler loading. The clean CENs are, as expected, showing higher decomposition temperature values. Initial decomposition temperatures are higher in the case of unclean CENs since there are metal nanoparticles present .

4.3.3 Integral Procedural Decomposition Temperature (IPDT)

The “integral procedural decomposition temperature” (IPDT), was devised as a means of summing up the whole shape of the normalized data curve. As such, it is consistently available from the cumulative data record of thermogravimetric analysis in inert atmosphere.

Calculation of IPDT:

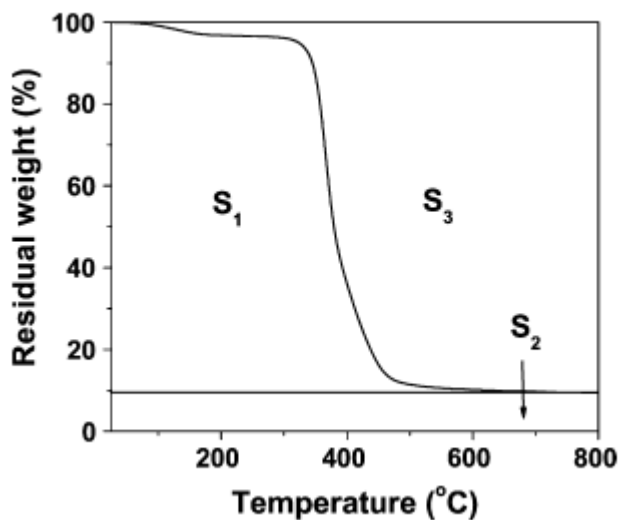


Figure 4.16. The schematic diagram of the Doyle's method for determining the IPDT [46]

$$\text{IPDT}(\text{°C}) = AK.(T_f - T_i) + T_i$$

$$A = (S_1 + S_2)/(S_1 + S_2 + S_3) \quad \text{and} \quad K = (S_1 + S_2)/S_1$$

Equation 4.1. IPDT calculation from Doyle's method [47]

The product AK represents a truly comprehensive index of intrinsic thermal stability.

materials which are highly refractory, but which begin to decompose at relatively low temperatures, have AK values which fall far short of their potential levels. Conversely, appropriately high AK values are found for some completely volatile materials which remain stable up to relatively high temperatures.

The areas S1, S2 and S3 in a TGA thermogram are schematically shown in Figure 4.15. .Where, T_i and T_f are the initial and final experimental temperatures, respectively.

Table 4.6. IPDT values of different nanocomposite samples

Filler type and wt %	IPDT (°C)
Neat epoxy (0%)	373.58
Unclean	
0.5 %	391.03
1 %	411.70
2 %	420.4
Clean	
0.5	398.21
1	417.05
2	428.27

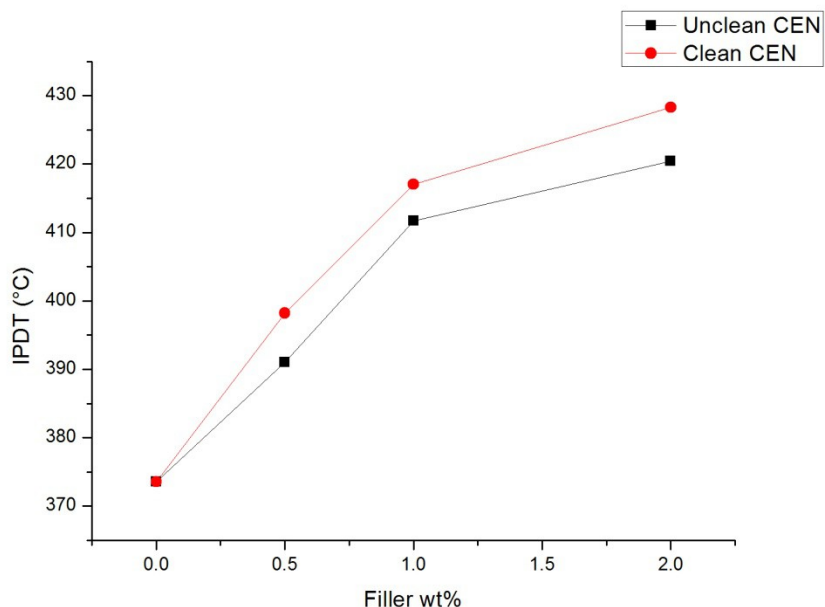


Figure 4.17. IPDT variation with filler wt % of Unclean and Clean CNT reinforced epoxy

In general, the thermosetting polymers have relatively large crosslinking density, which results in high decomposition temperature. Clean CEN have relatively better amount of CNTs and have clearly helped in increasing crosslinking density which is evident by the better IPDT values.

4.4. Comparison with neat epoxy resin

Here we try to compare all the best thermal and mechanical property in our analysis and match them up with neat epoxy resin to calculate the percentage improvement.

Table 4.7. Properties of neat epoxy resin along with maximum properties shown by the CEN

Property	Value (Neat epoxy resin)	Max. value for nanocomposite	Nanocomposite type	Improvement
Tensile strength	40.05	43.36	2 wt% unclean	+8.26 %

(MPa)				
Elastic modulus (MPa)	511	646	2 wt% unclean	+20.89%
Fracture toughness (MPa.m ^{1/2})	0.695	1.834	1 wt% unclean	+163.88%
Fracture energy (J/m ²)	51.145	165.771	1 wt% unclean	+224.11%
% elongation (tensile test)	9.05	11.26	2 wt% unclean	+2.21%
Glass transition temperature(°C)	54.48	67.96	2 wt% clean	+13.48 °C (+24.74%)
5 wt% decomposition temperature (°C)	235.36	288.35	1 wt% clean	+52.99 °C (+22.51 %)
10 wt% decomposition temperature (°C)	310.20	337.49	1 wt% clean	+27.29 °C (+8.79 %)
Onset temperature (°C)	311.19	338.26	1 wt% unclean	+27.17 °C (+8.73 %)
Offset temperature (°C)	450.11	482.90	1 wt% clean	+32.79 °C (+7.28 %)

Except fracture toughness, the mechanical properties have shown an increasing trend till 2 wt% CNT loading. On the other hand most thermal properties have attained their maximum values at 1 wt%. Further loading has led to a slight decrease in properties. The thermal properties are enhanced by better dispersion in the resin while the mechanical properties are improved by better interface adhesion. Thus it is clear that large agglomerates observed in the 2 wt% reduced the dispersion of CNTs but it still maintained strong adherence to the interface resulting in increased tensile strength and elastic modulus.

CHAPTER 5

CONCLUSIONS

- The tensile strength as well as Young's modulus is increasing with the particle loading. This result may be explained by the fact that the agglomerates in the untreated composites act as large particles and thus provide higher apparent filler loading. These agglomerates trap polymer in the void space between MWNT and effectively reduce the volume fraction of the epoxy matrix. Though it is worth noticing that there isn't a significant increase in both the values. This may be

due to the presence of high amount of nanobeads in the carbon nanoforms produced which has very less strength compared to carbon nanotubes and hence the not-so-substantial improvement.

- The neat epoxy resin has a fracture toughness of $K_{Ic} = 0.695 \text{ MPa m}^{1/2}$. Non-functionalised nanoparticles generally increase the fracture toughness of the epoxy matrix significantly at very low filler contents. The relative improvement of the K_{Ic} -value is not dependent on the particle-shape and, therefore, the main fracture mechanical mechanism leading to the enhanced fracture toughness could be related to the huge surface area of the nanoparticles. As we observed a partly agglomerated dispersion for all nanofillers, which leads to the conclusion that the localised inelastic matrix deformation void nucleation and crack deflection at the agglomerates are the dominating toughening mechanisms. For all mechanical characteristics, an exploitation of the theoretical surface area of the nanofiller as interface to the epoxy matrix is related to the dispersion and matrix impregnation. Thus, the interface is playing a major role concerning toughening of materials. According to the mentioned toughening mechanisms, we suggest a combination of individually separated dispersed nanotubes and well-impregnated small (sub-micrometer) agglomerates to be a favourable state of dispersion. However, a too strong interfacial adhesion between matrix and reinforcement negatively affects the toughness by suppressing interfacial failure, which is prerequisite for many toughening mechanisms.
- Assuming that the carbon nanoforms in the composite have a certain level of nanotubes present have extremely large surface area and they are at the same scale of the resin molecules. Interactions between tubes and resin molecules are expected to be intensive. Therefore, the resin molecules segment movement may intensively interact with the CNTs and consume energy. These intensive molecular-level interactions may be the major reason to result in the increase in T_g for the CNT epoxy nanocomposites. After acid cleaning the nanoforms will have a higher percentage of nanotubes which is evident from the better T_g values of clean CNT/epoxy composite.
- The thermal stability is increasing with filler loading that may be due to presence of good dispersion that helps in cross linking to some level. The crosslink density is maximized when the complete stoichiometry of the epoxy is maintained. If the stoichiometry of epoxy matrix is broken due to the formation of agglomerates, the crosslinking density would be reduced. But in our case

the probable higher crosslinking density resulted in higher decomposition temperature.

- IPDT is increasing with the filler loading and since it is a measure of decomposition temperature, this is expected (as mentioned above).

In a nutshell, we can say that the matrix structure, interfacial bonding and well dispersion of particle by optimizing mixing parameters are very important for a particular type of nano-filler and epoxy combination to enhance the properties of matrix. There are a few suggestions for improvement:-

1. Higher yield of carbon nanotubes can be attained by monitoring the acetylene flow rate to a minimum during the chemical vapor deposition process. A higher operating temperature can also provide favourable yield with more percentage of SWCNTs, which have shown better mechanical properties when reinforced into epoxy.
2. Literature has reported functionalization of nanotubes improving interfacial adhesion and dispersion in the matrix leading to better thermal and mechanical properties. We already observed this in case of thermal properties of acid cleaned CEN (Acid cleaning using HNO_3 leads to $-\text{OH}$ functionalization). Using cleaned nanoforms also increases the percentage of CNTs in the filler hence improving properties.
3. As we observed agglomerates were still present in the samples of high nanoform weight percentage (2 wt. % in our case) so, there are some limitations of ultrasonic mixing in breaking agglomerates. So, further work can be done by using improved ultrasonic mixing or any other method.
4. Since some properties in our case have either dipped (fracture toughness) or shown very little improvement (tensile strength) when reaching 2 wt% filler loading, it is advisable to not go further, taking both economy and property improvement into perspective.

CHAPTER 6
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