

PERFORMANCE EVALUATION OF CARBON NANOTUBES MODIFIED FIBRE REINFORCED POLYMER COMPOSITES

A

Thesis

Submitted in fulfillment of the requirement

for the award of degree of

DOCTOR OF PHILOSOPHY

By

MOHIT GARG

(Registration No. - 951208006)

Under the supervision of:

Dr. Rajeev Mehta

Professor

Department of Chemical Engineering

Thapar University, Patiala

Dr. Shruti Sharma

Associate Professor

Department of Civil Engineering

Thapar University, Patiala



OCTOBER – 2016

This Thesis is dedicated to

My mentors, Rajeev Mehta and Shruti Sharma, who taught me the principle of life,

My parents, who never stop giving of themselves in countless ways,

My beloved wife, who lead me through the valley of darkness with light of hope and support,

My dearest brothers, who always encouraged and supported me,

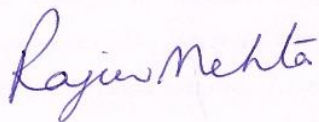
My friends, relatives and in-laws who stood by me when things look bleak.

You all have successfully made me the person I am becoming

You will always be remembered and cherished throughout my life

CERTIFICATE

This is to certify that the thesis entitled, **“PERFORMANCE EVALUATION OF CARBON NANOTUBES MODIFIED FIBRE REINFORCED POLYMER COMPOSITES”** submitted by **Mr. Mohit Garg** for the fulfillment of the requirements of the award of Degree of ‘Doctor of Philosophy’ in the Department of Mechanical Engineering, Thapar University, Patiala, is a record of the candidate’s own work carried out by him from July 2012 to June 2016 in this university under our supervision. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any university or institute.



(Dr. Rajeev Mehta)

Professor

Department of Chemical Engineering

Thapar University, Patiala



(Dr. Shruti Sharma)

Associate Professor

Department of Civil Engineering

Thapar University, Patiala

ACKNOWLEDGEMENT

First and foremost, I would like to thank the almighty whose countless blessings have made me who I am today. He enabled me with philosophy, perception and motivation to present this work, after handling the tough times with empathy, professionally and clarity.

During the course of this thesis several personnel directly or indirectly contributed in making this doctoral dissertation possible and I will always remain deeply indebted to them.

Firstly, from the core of my heart, I would like to express special thanks to my esteemed supervisors, Dr. Rajeev Mehta (Professor) and Dr. Shruti Sharma (Associate professor) for encouraging my research and for allowing me to grow as a research scientist. Their consistent support, dynamic supervision, valuable and innovative suggestions have enlightened my knowledge and skills in the area of nanocomposites and structural health monitoring. Both of them have been a tremendous mentor now and forever.

Besides my supervisors, I wish to express humble and special thanks to Prof. S.K. Mohapatra and Prof. Ajay Batish for providing me necessary facilities in the department along with their encouragement and constant moral support to accomplish this task. I would also like to acknowledge the valuable suggestions of the members of the Doctoral Committee, Dr. Tarun Kumar Bera, Dr. Naveen Kwatra and Dr. Vivek Jain for their insightful comments and questions, during my presentations. I sincerely appreciate the whole hearted co-operation and valuable help rendered by teaching and non-teaching staff of the Department of Mechanical Engineering (MED), Thapar University.

I am grateful to Dr. Sandeep Sharma, who provided me the experimental set-up to carry out my research work and valuable guidance over the past four years. Without his benevolent motivation and support it would not have been possible to conduct this research. I am also thankful to Dr. J.S. Saini, Dr. Tarun Nanda, and Mr. Kishore Khanna, for their motivational and true advice. A thanks also goes to Dr. O.P. Pandey, Dean of Research and Sponsored Projects for providing the possible research facilities.

I thank my seniors Mr. Bikramjit Sharma and Dr. Shilpa Narang, along with fellow research scholars, Mr. Karanbir Singh and Mr. Ashutosh Sharma with whom I have spent these years of research and enjoyed many interactive sessions.

I am also thankful to all the laboratory staff members, who maintained all the machines, sources and equipments so efficiently, which helped me in performing experiments accurately.

The financial assistance rendered by Naval Research Board (NRB), India for carrying out experimental work and characterization of samples is gratefully acknowledged. Their financial support acted like a catalyst that helped me in achieving tremendous results in my research. I am thankful to the faculty of Mechanical Department who gave me an opportunity to share my knowledge as teaching assistant during this research period.

A special thanks is also due for my family, words cannot express how grateful I am to my parents for all their sacrifice that they had made on my behalf and who have always been my strongest support and my source of motivation during moments of despair and discouragement. I would also like to thank my brothers for providing support and refreshing me during the hardships to strive towards the goal. Finally, I would like to thank the better-half, my wife, Dr. Gurvinder Kaur Garg, who has been a constant source of strength and inspiration. I also admire her suggestions which have helped me to iron out the creases in my thesis. This thesis would not have been possible without her unconditional and unending love, support and cooperation as a friend and wife. She has always taken my problems as her own, and helped me to overcome them, and encouraged me to achieve a unique level. Thanks to her for her faithful love and endless guidance. I could say, without her, this thesis wouldn't exist.

I want to thank my relatives and friends who have supported me by any means over the past four years in my pursuit of completing my Doctoral Degree. Special thanks to Dr. Mona Batish, in US, for her consistent efforts in providing me access to the latest journal articles.

I extend my special thanks to all who kept me well-balanced and have tried to make this challenging task a pleasant journey.

Patiala

October, 2016.


(Mohit Garg)

ABSTRACT

The present study is carried out to reinforce glass fibre polymer composites using nano-fillers, which facilitate enhanced mechanical performance as well as durability in hygrothermal environment. Also, the study proposes a non-contact, non-invasive, *in-situ* damage monitoring methodology to identify the defects introduced in composite laminates either during the manufacturing stage, while in-service or after exposure to hygrothermal conditions.

The Glass-fibre reinforced polymer (GFRP) composites form an important topic of research and are widely used for preparing components of marine structures such as canoes, fishing trawlers, patrol boats and naval mine-hunting ships. This is attributed to the fact that GFRP composites possess high strength-to-weight ratio, lower initial and maintenance costs, and excellent corrosion as well as thermal resistance as compared to traditional materials such as steel or aluminum. Apparently, the marine components consist of glass fibre mat strongly bonded by means of a thermosetting matrix, usually the epoxy resin which has excellent properties such as low shrinkage after curing, good resistance to corrosion and stability at higher temperatures.

However, with recent advancement in technology, the GFRP composites are being replaced with nanocomposites, which have exceptionally high surface-area-to-volume ratio as well as high aspect ratio. For preparing nanocomposites the nano-fillers are dispersed into the matrix during the processing phase and are usually added by weight percentage of the order of 0.5 – 5%. Studies have confirmed that relatively lower loading of nano-fillers is sufficient to obtain composites with desired properties as compared to those obtained with higher loading of micro-fillers. There are several nano-fillers that are incorporated globally to develop multifunctional composite materials with outstanding properties. The commonly used nano-fillers are nanoclay, graphene, carbon nanofibers, and carbon nanotubes. Amongst these, carbon nanotubes (CNTs) have been the most promising nanofiller which appear as long and thin cylinders of carbon, when observed under the microscope. Due to their unique combination of physical and multifunctional properties, CNTs have become a strong candidate for use as tailoring agents in various polymer matrices to develop advanced composite materials for the 21st century.

In view of these observations, the present study addresses the enhancement in mechanical properties of GFRP composites at the macro-scale by treating the glass fibres with silane coupling agents and at the nanoscale by reinforcing the matrix using carbon nanotubes. It has been observed experimentally that by treating the glass fibre mat with amino and epoxy silane coupling agents, in neat epoxy (EP) matrix composition, the flexural strength improved by 139% and 125%, respectively. This was possibly due to enhanced interfacial bonding between the fibre and the epoxy matrix. The experimental results also revealed that the silanization of glass fibres benefited the flexural properties more than the tensile properties of neat epoxy and CNT modified epoxy matrix compositions.

In addition, the present study also reports an effective and stable methodology for dispersion of carbon nanotubes in epoxy resin. Interestingly, for the first time, the pristine nanotube modified (PCNT) GFRP composites have scored over, amino-functionalized nanotube (ACNT) GFRP composites when prepared at stoichiometric ratio. This is a very significant finding since PCNT is available at a much lower cost than ACNT. Further, it has also been observed that dispersion of ACNT in an amine-rich concentration proved advantageous over EP GFRP and PCNT GFRP composites. This may be due to stronger cross-linking network and interfacial bonding that was evident from the composite mechanical behavior and also supported by SEM images. Lastly, for specific processing conditions the composite prepared by dual reinforcement, i.e at the macro-scale by treating fibre surface with amino silane and at the nanoscale by homogeneously dispersing ACNT in amine-rich resin demonstrated considerable increase in mechanical properties as compared to EP GFRP specimen.

The composite materials fabricated in this study were designed as a replacement of existing materials used for marine structures. Generally for marine application, the factors affecting the longevity, durability and performance of GFRP components are based on exposure to hygrothermal conditions. The rate of degradation of composite materials when exposed to different environmental conditions depends upon the intensity, duration and type of exposure, which makes it complex and rather difficult to predict. The physical/mechanical/chemical changes due to water absorption weakens the fibre-matrix interfacial bonding, initially visualized as delamination or micro cracking under the microscope, but on prolonged exposure causes failure of the composites. Hence, in order to investigate the performance of manufactured composites under submerged conditions, the EP GFRP, PCNT GFRP and ACNT GFRP samples

were exposed to simulated seawater (SW) environment at relatively lower and higher temperatures (25°C and 55°C). Subsequently, the weight gain, diffusivity rate and change in mechanical properties of the conditioned samples were evaluated. From the diffusion studies carried out at 25°C in SW and distilled water (DW), it was observed that the absorbed equilibrium moisture content and diffusivity rate for EP GFRPs was higher in DW than in SW. This has been attributed to the formation of the salt layer on the surface of samples immersed in SW (also depicted in SEM images) which in turn reduced the capillary flow of water into the interface. The plasticizing effect of water on material's stiffness and strength was observed to be significant during first 15-20 days but recovered over prolonged aging. Contrarily at elevated temperature, the water content in the EP GFRP composite increased at a faster rate and reached higher levels than observed at room temperature. Further, in order to assess the performance of CNT modified GFRP composites, the PCNT GFRP and ACNT GFRP samples were also exposed to SW environment. The exposure of the ACNT and PCNT GFRP composites at 55°C also resulted in higher water absorption as observed for EP GFRP samples. The excess water content in the composite proved to be detrimental as it induced swelling of the matrix and weakened the fibre-matrix interfacial bonding strength. It also led to early occurrence of damages such as crack formation, stress concentration sites, fibre-delamination, etc., thus affecting the stability and performance of the composite.

Interestingly, from the diffusion study carried out at 25°C in SW it was observed that the absorbed water content and diffusivity rate plunged by about 35% due to the presence of CNTs in an epoxy matrix. This is possibly due to the barrier properties of CNTs wherein, the individual CNTs spread to nano-level in the entire material, thus offer a tortuous path to the diffusing water molecules. Further, the flexural properties of ACNT GFRP samples dropped initially, but, showed a recovery after approximately 30 days of immersion and the possible reasons explaining it have been discussed in the chapters ahead. On the contrary, PCNT GFRP samples illustrated a continuous drop in stiffness, strength, and ductility with an increase in aging time in SW. It may be stated that ACNT GFRP composites showed better performance than EP GFRP composites on immersion in SW.

Further, from SEM images it was observed that the exposure of GFRP composites in SW (which represents actual service conditions) caused frequent fibre breakage, delamination, cracks and surface abrasion. In addition to service induced damages, some defects (such as air gaps,

missing epoxy) were also introduced during manufacturing of GFRP composites. Thus, a health monitoring tool was needed to assess such damages/defects in GFRPs so that the failure of the composite structures could be prevented. Amongst various non-destructive tools (NDT), ultrasonic guided waves had shown a better response to defects in thin-plate-like structures under submerged conditions and also emerged as an effective health monitoring tool. Interestingly, guided wave mode specific for GFRP laminates was excited and the ultrasonic signal was recorded in healthy and defective regions. The leaky Lamb waves that propagated through the GFRP sheet were able to identify, quantify the presence and severity of defects/damages such as air gaps, missing epoxy, notches and surface abrasion. In general, the ultrasonic signal strength dropped for manufactured as well as usage defects in GFRP laminate.

The developed methodology was reliable as it showed reproducibility of results on monitoring usage defects (i.e. notches and surface degradation) in CNT GFRP laminate. In addition to this, the developed *in-situ*, non-contact and non-invasive structural health monitoring technique was also successful in diagnosing defects introduced in EP GFRP sheet after exposure to warm seawater conditions. It is important to point out that, a linear relation between the drop in ultrasonic voltage amplitude, tensile strength, and increasing water uptake content over immersion time was successfully established in this study.

The non-destructive damage monitoring technique developed for composite structures in this study allows the inspection of the component without interfering with its service conditions, thus providing an excellent balance between quality control and cost-effectiveness. Therefore, the *in-situ*, non-contact and non-invasive Lamb wave technique can serve as an effective method to diagnose the service life of a structural component made up of composite while, they are in operational mode.

LIST OF PUBLICATIONS

The results incorporated in this thesis are fully documented. The following publications in peer reviewed SCI journals have come out of the work carried out. Some of the work has also been presented at national/international conferences/seminars.

International SCI Journals

5 – Published

- Role of curing conditions and silanization of glass fibers on carbon nanotubes (CNT) reinforced glass fiber epoxy composites; **Mohit Garg**, Shruti Sharma, Rajeev Mehta; Composite Interfaces, 24(2), **2016**: 233-253 (**IF: 0.726**)
- Carbon nanotube-reinforced glass fiber epoxy composite laminates exposed to hygrothermal conditioning; **Mohit Garg**, Shruti Sharma, Rajeev Mehta; Journal of Materials Science, 51(18), **2016**: 8562-8578 (**IF: 2.371**)
- Processing of functionalized and pristine carbon nanotube epoxy composites with silane treated glass fiber, **Mohit Garg**, Shruti Sharma, Rajeev Mehta; Material and Manufacturing Processes, 31(15), **2016**: 2044-2056 (**IF: 1.629**)
- Non-contact damage monitoring technique for FRP laminates using guided waves, **Mohit Garg**, Shruti Sharma, Sandeep Sharma, Rajeev Mehta; Smart Structures and Systems, 17(5), **2016**: 795-817 (**IF: 1.268**)
- Pristine and amino functionalized carbon nanotube epoxy composites, **Mohit Garg**, Shruti Sharma, Rajeev Mehta, Composites Part A, 76, **2015**: 92-101 (**IF: 3.017**)

1 – Under review

- Effect of processing conditions on the mechanical behavior of amino functionalized nanotube modified glass fiber epoxy composites; **Mohit Garg**, Shruti Sharma, Rajeev Mehta; Journal of Current Science. (**IF: 0.786**)

1 – Ready for communication

- Study of effect of hygrothermal aging of GFRP composites using destructive and non-destructive techniques; **Mohit Garg**, Shruti Sharma, Sandeep Sharma, Rajeev Mehta.

1 – In preparation

- Review paper on CNT reinforced glass fiber composites; **Mohit Garg**, Shruti Sharma, Rajeev Mehta

Papers in conference proceedings

- Review of carbon nanotube modified fiber reinforced polymer composites, **Mohit Garg**, Shruti Sharma, Rajeev Mehta, ICAPM 2013 Proceedings, 11–13 Oct, 2013.
- Mechanical properties of polymer nanocomposites, **Mohit Garg**, Shruti Sharma, Rajeev Mehta, ICPC 2014 Proceedings, 19-21 Dec, 2014.
- Processing of polymer nanocomposites containing Carbon nanotubes, **Mohit Garg**, Shruti Sharma, Rajeev Mehta, ICPC 2014 Proceedings, 19-21 Dec, 2014.

ABBREVIATIONS USED

ACNT	Amino functionalized nanotubes
AR	as-received
AS (commercial name APS)	3-aminopropyltriethoxy silane
ASGF	Amino silane treated glass fibre
ASTM	American Society for Testing and Materials
CNT	Carbon nanotube
CVD	Chemical vapor deposition process
DGEBA	Diglycidyl ether of bisphenol-A
DSC	Differential scanning calorimetry
DW	Distilled water
DWCNT	Double walled carbon nanotube
EDS	Energy-dispersive-spectroscopy
EP	Neat epoxy
ES (commercial name GPS)	3-Glycidyloxypropyltrimethoxy silane
ESGF	Epoxy silane treated glass fibre
FRP	Fibre reinforced polymer/plastic
FTIR	Fourier transform infrared spectrometer
GF	Glass fibre
GFRP	Glass fibre reinforced polymer/plastic
GPa	Giga-Pascal's
HT	Heat treated glass fibres
IFSS	Interfacial shear strength
ILSS	Interlaminar shear strength/stress
MWCNT	Multi walled carbon nanotube
mPa	Milli-Pascal
MPa	Mega-Pascal's
NDT	Non-destructive testing
PCNT	Pristine nanotubes without any functionalization

PNC	Polymer nanocomposite
PT	Pulse transmission mode
PZT	Lead Zirconate Titanate transducer
RH	Relative humidity
RT	Room temperature
rpm	revolutions per minute
RTM	Resin transfer molding
SEM	Scanning electron microscopy
SA	Surface area
SSA	Specific surface area
SW	Seawater
TEM	Transmission electron microscope
TGA	Thermo gravimetric analyzer
T _g	Glass transition temperature
TOF	Time-of-flight
TPa	Tera-Pascal's
UT	Ultrasonic testing
UGW	Ultrasonic guided waves
VARIM	Vacuum assisted resin infusion molding
VARTM	Vacuum assisted resin transfer molding

NOMENCLATURE

S. No.	Nomenclature	Description
1.	EP GFRP	Neat epoxy (0.0 wt% CNT) glass fibre reinforced polymer composite
2.	EP ASGFRP	Amino silane treated glass fibre reinforced with neat epoxy matrix
3.	EP ESGFRP	Epoxy silane treated glass fibre reinforced with neat epoxy matrix
4.	CNT GFRP	Carbon nanotube modified glass fibre reinforced polymer composite
5.	CNT/Epoxy	A mixture of epoxy resin in which carbon nanotubes (either pristine or amino functionalized) are dispersed
6.	ACNT GFRP	0.1 wt% amino functionalized nanotube glass fibre reinforced polymer composite
7.	PCNT GFRP	0.1 wt% pristine (non-functionalized) nanotube glass fibre reinforced polymer composite
8.	ACNT ARGFRP	As-received glass fibre reinforced with ACNT matrix
9.	ACNT ASGFRP	Amino silane treated glass fibre reinforced with ACNT matrix
10.	ACNT ESGFRP	Epoxy silane treated glass fibre reinforced with ACNT matrix
11.	PCNT ASGFRP	Amino silane treated glass fibre reinforced with PCNT matrix
12.	PCNT ESGFRP	Epoxy silane treated glass fibre reinforced with PCNT matrix

TABLE OF CONTENTS

CERTIFICATE.....	iii
ACKNOWLEDGEMENT.....	iv
ABSTRACT.....	vi
LIST OF PUBLICATIONS	x
International SCI Journals.....	x
Papers in conference proceedings	xi
ABBREVIATIONS USED	xii
NOMENCLATURE.....	xiv
LIST OF FIGURES.....	xix
LIST OF TABLES.....	xxvii
Chapter 1. Introduction	1
1.1 GFRP composites.....	1
1.2 CNT modified GFRP composites	5
1.3 Silane treatment of glass fibres	10
1.4 Hygrothermal aging.....	13
1.5 Damage monitoring in GFRP laminates	16
1.6 Outline of thesis	18
Chapter 2. Literature review	22
2.1 CNT modified GFRP composites	22
2.2 Silane treatment of glass fibres	48
2.3 Hygrothermal aging of GFRP composites	67
2.4 Health monitoring of FRPs using ultrasonic guided waves	89
2.5 Closing remarks.....	103
2.6 Gaps in the literature	103
2.7 Objectives of thesis	104
Chapter 3. CNT modified GFRP composites	105
3.1 Introduction	105
3.2 Materials.....	105
3.3 Methodology	105
3.3.1 CNT modified GFRP composites.....	105

3.3.1.1	Preparation of neat epoxy mixture	107
3.3.1.2	Dispersion of CNT into epoxy resin	108
3.3.2	Fabrication of laminates using VARIM	109
3.3.3	Characterization.....	110
3.4	Results and Discussion.....	112
3.4.1	Incorporation of nanotubes as reinforcement in EP GFRP composites	112
3.4.1.1	Polymerization and TEM analysis	113
3.4.1.2	Mechanical behavior of CNT GFRP composites at stoichiometric ratio.....	119
3.4.1.3	Effect of resin: hardener ratio.....	126
3.4.1.4	Effect of processing techniques on dispersion of CNT in epoxy matrix	134
3.4.1.5	Effect of resin temperature during infusion on mechanical properties	139
3.5	Closing remarks.....	143
	Chapter 4. Surface treatment of glass fibres	144
4.1	Introduction	144
4.2	Materials and Methodology	145
4.2.1	Materials	145
4.2.2	Methodology.....	145
4.2.2.1	Heat treatment	146
4.2.2.2	Epoxy silane treatment	147
4.2.2.3	Amino silane treatment	147
4.2.2.4	Characterization	148
4.2.3	Rationale for choosing silane coupling agents	149
4.3	Results and Discussion.....	152
4.3.1	Mechanical behavior.....	152
4.3.2	FTIR and SEM analysis.....	161
4.3.3	Effect of ACNT dispersion in amine hardener versus resin	165
4.3.4	Composite with optimal matrix and silane treatment	168
4.4	Closing remarks.....	171
	Chapter 5. Hygrothermal aging of composites.....	172
5.1	Introduction	172
5.2	Experimental set-up.....	175
5.3	Methodology	177
5.3.1	Calculating water uptake content and diffusivity rate	177

5.3.2	Hygrothermal conditions	179
5.3.3	Characterization.....	179
5.4	Results and discussion.....	180
5.4.1	Diffusion studies.....	180
5.4.1.1	CNT modified GFRP composites at room temperature	180
5.4.2	Performance evaluation	186
5.4.2.1	EP GFRP composites	186
5.4.2.1.1	FTIR analysis of the aging process.....	191
5.4.2.2	CNT modified GFRP composites	193
5.4.2.2.1	PCNT GFRP composites	198
5.4.3	Effect of edge coating on water infusion behavior for GFRP samples	203
5.4.3.1	Effect of edge coating on ACNT GFRP composites.....	207
5.4.4	Degradation of composites at different temperatures.....	210
5.4.4.1	ACNT GFRP composites at 55°C and 25°C temperatures.....	210
5.4.4.2	PCNT GFRP composites at 25°C and 55°C temperatures	212
5.4.4.3	Silane treated GFRP samples at 25°C and 55°C temperatures.....	214
5.5	Closing remarks.....	221
Chapter 6. Damage monitoring in GFRP laminates		223
6.1	Introduction	223
6.2	Methodology	224
6.3	Set-up and specimen details	225
6.4	Generation of specific leaky Lamb waves in EP GFRP laminate.....	229
6.4.1	Selection of optimum distance of separation (D_s)	229
6.4.2	Selection of optimum angle (θ)	231
6.4.3	Selection of optimum propagation span (P_s)	233
6.5	Defect detection using Guided waves	238
6.5.1	Manufacturing defects	238
6.5.1.1	Air gaps	240
6.5.1.2	Missing epoxy	240
6.5.2	Usage defects (simulated).....	241
6.5.2.1	Notches and surface defects	241
6.6	Results and discussion.....	244

6.6.1	Presence of air gap.....	244
6.6.2	Missing epoxy.....	246
6.6.3	Notches and surface defects	249
6.7	Methodology validated in CNT GFRP laminate.....	253
6.8	NDT of hygrothermal specimen.....	258
6.8.1	Results and discussion	258
6.8.1.1	Destructive tests	258
6.8.1.2	Guided wave investigations	261
6.9	Closing remarks.....	266
Chapter 7. Optimal curing conditions of CNT modified GFRP composites		268
7.1	Introduction	268
7.2	Characterization	270
7.3	Results and discussion.....	271
7.3.1	Effect of CNT on the curing process	271
7.3.1.1	Effect of optimal curing schedule on mechanical behavior of ACNT GFRP... ..	277
7.3.2	Effect of implementing optimal curing schedule on different GFRP compositions	279
7.3.2.1	EP GFRP composition	279
7.3.2.2	Effect of silane treatment of glass fibres in ACNT and PCNT matrix	283
7.4	Closing remarks.....	291
Chapter 8. Conclusion and Recommendations for future work		292
8.1	CNT modified GFRP composites	292
8.2	Silane treatment of glass fibres	293
8.3	Hygrothermal aging.....	294
8.4	Damage monitoring in GFRP laminates	296
8.5	Optimal curing conditions of CNT GFRP composites.....	297
8.6	Future scope of work.....	298
References		299

LIST OF FIGURES

S. No.	Caption	Page No.
Figure 1.1:	A schematic diagram that compares the particle and matrix interaction in nanocomposites and micro-composites [Source: Li Y <i>et al.</i> , 2010]	4
Figure 1.2:	Three different types of carbon nanotubes a) single walled b) multi-walled c) double walled. [Source: Harris, (1999)]	6
Figure 1.3:	TEM image showing the structure of a MWCNT	7
Figure 1.4:	Schematic representation of silane coupling agents	11
Figure 1.5:	Hydrolysis process of silane coupling agents [Source: Zhao <i>et al.</i> , 2012]	12
Figure 2.1:	(a) Relative orientation of transmitter, receiver and plate specimen, (b) schematic diagram of the internal defects in five layers of the composite plates specimen [Source: Kundu <i>et al.</i> , 2001]	90
Figure 2.2:	Structure of the GLARE3-3/2 composite and the position of the defect [Source: Demcenko <i>et al.</i> , 2005]	92
Figure 3.1:	Chemical structure of DGEBA resin	106
Figure 3.2:	Reaction between epoxy resin and amine hardener	106
Figure 3.3:	Schematic diagram of CNT GFRP composite preparation	108
Figure 3.4:	VARIM equipment for fabricating GFRP laminates	109
Figure 3.5:	Schematic representation of the materials and equipments utilized in the preparation of GFRP composite laminates	110
Figure 3.6:	SEM picture of as-received MWCNT-NH ₂ at magnification of 500x (A) and 1000x (B), [Source: Rahman <i>et al.</i> , (2012)]	113
Figure 3.7:	FTIR spectra of (a) Neat epoxy liquid sample, (b) EP GFRP composite, (c) ACNT GFRP composite	114-115

Figure 3.8:	TEM image showing dispersion of 0.1wt% ACNT in epoxy resin	117
Figure 3.9:	Mechanism of reactions between ACNT and epoxide group [Source: Hossain <i>et al.</i> , 2014]	118
Figure 3.10:	Effect of CNT composition on the tensile and flexural strength	120
Figure 3.11:	SEM image of fractured surface of tensile specimens of: (a) PCNT GFRP and (b) ACNT GFRP composites	121
Figure 3.12:	Effect of CNT composition on the tensile and flexural modulus	122
Figure 3.13:	Stress-strain behavior with the addition of nanotubes in EP GFRP composites: Tensile loading	123
Figure 3.14:	Stress-strain behavior with the addition of nanotubes in EP GFRP composites: Flexural loading	125
Figure 3.15:	Stress-strain behavior for ACNT GFRP and PCNT GFRP composites in amine-rich resin matrix: Tensile loading	130
Figure 3.16:	Fracture surfaces of: (a) EP GFRP (76% resin), (b) ACNT GFRP (76% resin), (c) PCNT GFRP (76% resin), (d) ACNT GFRP (69% resin) and (e) PCNT GFRP (69% resin)	131-133
Figure 3.17:	Effect of processing techniques on the modulus of CNT reinforced composites	136
Figure 3.18:	Effect of processing techniques on the strength of CNT reinforced composites	137
Figure 3.19:	TEM images showing (a) dispersion of 0.1 wt% ACNT in epoxy resin, (b) homogeneous dispersion of ACNT in epoxy resin after sonication	138
Figure 3.20:	Effect of polymer mixture temperature on EP GFRP and ACNT GFRP composites: Modulus	140
Figure 3.21:	Effect of polymer mixture temperature on EP GFRP and ACNT GFRP composites: Strength	141
Figure 3.22:	Effect of polymer mixture temperature on EP GFRP and ACNT GFRP composites: ILSS	141

Figure 3.23:	Effect of different infusion temperature on Stress versus Strain relationship for ACNT GFRP composites	142
Figure 4.1:	Chemical structure of (a) GPS and (b) APS silane coupling agents	146
Figure 4.2:	(a) Surface treatment of glass fibres with amino silane coupling agent; (b) schematic representation of a possible structure for amino silane coating on glass fibre	148
Figure 4.3:	Schematic representation of the possible interactions among the various hybrid material constituents	151
Figure 4.4:	Effect of heat and amino silane treatment of glass fibre mat in neat epoxy on tensile and flexural properties studied through (a) modulus, (b) strength	153
Figure 4.5:	Effect of heat and silane treatment of GF in ACNT matrix on tensile and flexural modulus (1: ARGF; 2: AS(HT)GF; 3: ASGF; 4: ES(M)GF; 5: ES(M,HT)GF; 6: ES(E)GF; 7: ES(E,HT) GF)	156
Figure 4.6:	Effect of heat and silane treatment of GF in ACNT matrix on tensile and flexural strength (1: ARGF; 2: AS(HT)GF; 3: ASGF; 4: ES(M)GF; 5: ES(M,HT)GF; 6: ES(E)GF; 7: ES(E,HT) GF)	158
Figure 4.7:	FTIR spectra of (a) ACNT ASGFRP composite (shown by solid line) and (b) ACNT ARGFRP composite (shown by dotted line)	162
Figure 4.8:	Fracture surface of (a) ACNT ASGFRP, (b) ACNT ESGFRP samples	163-164
Figure 4.9 :	SEM images of (a) ACNT dispersion in resin and (b) ACNT dispersion in hardener	167
Figure 4.10:	Behavior of stress as a function of strain for ACNT ASGFRP composites (69%, optimal processing conditions) as compared to other ACNT GFRP composites	170
Figure 5.1:	Hygrothermal aging of EP GFRP and CNT GFRP samples on immersion in water bath when studied in a seawater environment	176
Figure 5.2:	Water uptake behavior of EP GFRP and CNT GFRP composites on exposure to seawater at 25°C	182

Figure 5.3:	Water uptake behavior of EP GFRP and CNT GFRP composites on exposure to distilled water at 25°C	183
Figure 5.4:	Effect on flexural properties of EP GFRP specimens after immersion in SW and DW for increasing aging time	187
Figure 5.5:	Damage on fibre-matrix interface after 360h (15 days) of immersion in (a) SW and (b) DW	188
Figure 5.6:	Reaction mechanism between cured epoxy resin and sodium ions from SW	189
Figure 5.7:	SEM image illustrating the morphology of EP GFRP specimens after 90 days exposure in (a) SW and (b) DW	190-191
Figure 5.8:	Changes in the FTIR spectra of EP GFRP composites during SW aging for (a) 0 days; (b) 15 days; (c) 30 days and (d) 90 days	192
Figure 5.9:	Effect on flexural properties of ACNT GFRP specimens after immersion in SW and DW for increasing aging time	195
Figure 5.10:	SEM image illustrating the morphology of ACNT GFRP specimens after aging in SW for 15, 30 and 90 days	196
Figure 5.11:	SEM image illustrating the morphology of ACNT GFRP specimens after aging in DW for 30 and 90 days	197
Figure 5.12:	Comparison between flexural properties of ACNT and PCNT GFRP samples after aging in SW for different immersion times	200
Figure 5.13:	Morphology of hygrothermal aged specimens after 2904h (121 days) for PCNT GFRP samples	202
Figure 5.14 :	Diffusion curves of EP GFRP composite (single and double epoxy coated) specimens immersed in: (a) SW, (b) DW	204
Figure 5.15:	Comparison of mechanical properties for EP GFRP composites (SW) – single versus double edge coating	206
Figure 5.16:	Diffusion behavior of ACNT GFRP samples (SW) with single and double edge coating	207
Figure 5.17:	Mechanical behavior of ACNT GFRP, SC samples (SW) with	208

	immersion time upto 121 days	
Figure 5.18:	Mechanical behavior of ACNT GFRP, DC samples (SW) with immersion time up to 121 days	209
Figure 5.19:	Percent change in mechanical properties of ACNT GFRP composites after 15, 30 and 90 days aging in SW at 55°C	212
Figure 5.20:	Percent change in mechanical properties of PCNT GFRP composites after 15, 30 and 90 days aging in SW at 55°C	213
Figure 5.21:	Percent weight gain by silane treated GFRP laminates for varying immersion time in SW at 55°C	214
Figure 5.22:	Percent change in mechanical properties after 15, 30 and 90 days aging in SW at 55°C for (a) EP ESGFRP; (b) EP ASGFRP; (c) EP GFRP composites	216-217
Figure 6.1:	Experimental set-up (a) Actual; (b) Schematic arrangement	225-226
Figure 6.2:	Ultrasonic testing set-up	227
Figure 6.3:	Configuration of JSR Pulse Generator	228
Figure 6.4:	Quantitative and qualitative performance evaluation carried out on prepared CNT modified GFRP laminates	229
Figure 6.5:	Effect of time of flight of guided wave in water medium (a) Specimen PT signature; (b) Trends of transmitted voltage amplitudes with varying propagation span for $\theta = 24^\circ$	230
Figure 6.6:	(a) PT signatures at different angles of incidence; (b) Trends of V_p ($0^\circ - 32^\circ$)	232-233
Figure 6.7:	(a) Pulse transmission loss over propagation span length; (b) Effect on PT signatures by varying propagation span; (c) Trends of transmitted pulses with increasing span	234-235
Figure 6.8:	Time of flight versus propagation span at 24° in healthy region	236
Figure 6.9:	Sample PT signature to calculate group velocity theoretically	237
Figure 6.10:	Photograph of actual EP GFRP sheet with manufacturing defects (air gaps and missing epoxy) and in-service damages (notches and	243

	surface defects)	
Figure 6.11:	Effect on PT signatures with air gap locations (A1-A4) vis-à-vis healthy region	245
Figure 6.12:	Trends of normalized transmitted pulse voltages with presence of air gaps	246
Figure 6.13:	Effect on PT signatures with missing epoxy (D1-D3) vis-à-vis healthy signal	247
Figure 6.14:	Trends of normalized transmitted pulse voltages with different missing epoxy defects	248
Figure 6.15:	Effect on PT signatures with notches (N1-N3) vis-à-vis healthy signal	249
Figure 6.16:	Trends of normalized transmitted pulse voltages with different notch depth and orientation	250
Figure 6.17:	Effect on PT signatures with surface defect (S1-S4) vis-à-vis healthy signal	251
Figure 6.18:	Trends of normalized transmitted pulse voltages with different surface defects	252
Figure 6.19:	(a, b) Actual photograph of CNT GFRP laminate depicting usage defects (notches and surface abrasion)	254
Figure 6.20:	Effect on PT signatures: (a) with notches (N1- N2), (b) surface defects (S1-S3) vis-à-vis healthy signal	255-256
Figure 6.21:	Trends of normalized transmitted pulse voltages with different surface defects	257
Figure 6.22:	Tensile properties of EP GFRP specimens both unaged (reference) and immersed in SW for over 60 days: (a) modulus, (b) strength and strain at break	259-260
Figure 6.23:	Ultrasonic signatures in specimens exposed to SW after: (a) 7 days, (b) 15 days, (c) 30 days, (d) 60 days of immersion	261-263
Figure 6.24:	Percentage drop in ultrasonic signal strength of EP GFRP	264

composites on increasing seawater immersion time

Figure 6.25:	Comparison of ultrasonic signal strength with % weight gain in EP GFRP specimens up to 60 days of immersion	265
Figure 6.26:	Comparison of tensile strength, strain and Vp with increasing SW immersion	266
Figure 7.1:	Illustrating the mechanism of etherification reaction [Source: Saeb <i>et al.</i> , 2013]	269
Figure 7.2:	DSC thermograms for EP GFRP sample at heating rate of 10°C/min (First, second and third cycle)	271
Figure 7.3:	DSC thermogram for ACNT GFRP samples at heating rate 10°C per min (First, second and third cycle)	272
Figure 7.4:	TEM image depicting uniform dispersion and strong interfacial bonding of amino-CNTs with epoxy resin	273-274
Figure 7.5:	DSC thermograms for ACNT GFRP specimen cured for 10 h at 70°C	275
Figure 7.6:	DSC thermograms for ACNT GFRP specimen cured for 7 h at 85°C	276
Figure 7.7:	DSC thermograms for ACNT GFRP specimen cured for 10 h at 85°C	277
Figure 7.8:	Behavior of ACNT GFRP samples with varying curing schedules-Modulus	278
Figure 7.9:	Behavior of ACNT GFRP samples with varying curing schedules-Strength	278
Figure 7.10:	Effect of optimal curing conditions on EP GFRP composition (a) Modulus, (b) Strength	279-280
Figure 7.11 :	Morphology of EP GFRP composite cured for (a) 7h at 70°C (b) 7h at 85°C	281
Figure 7.12:	Comparison between EP GFRP and ACNT GFRP for optimal curing conditions (a) Modulus, (b) Strength	282-283
Figure 7.13:	Effect of optimal curing conditions on silane treated glass fibres in	284-285

ACNT matrix: (a) Modulus, (b) Strength

Figure 7.14:	Morphology of ACNT (a) ESGFRP and (b) ASGFRP samples cured for 7h at 85°C	286
Figure 7.15:	Effect of optimal curing conditions on silane treated glass fibres in PCNT matrix: (a) Modulus, (b) Strength	288
Figure 7.16:	Morphology of PCNT (a) ESGFRP and (b) ASGFRP samples cured for 7h at 85°C	290

LIST OF TABLES

S. No.	Heading	Page No.
Table 2.1:	Summary of literature review related to CNT modified FRP	31
Table 2.2:	Selected studies on reinforcement of silane treatment of glass fibres in either neat epoxy or CNT-modified epoxy matrix system	48
Table 2.3:	Summary of literature review related to polymer composites subjected to hygrothermal loading	71
Table 2.4 :	Summary of literature review related to polymer composites tested using UGW	95
Table 3.1:	Summary of mechanical properties obtained by modifying epoxy: hardener ratio for different GFRP compositions	127
Table 4.1:	Types of glass fibre treated samples in ACNT epoxy matrix	155
Table 4.2:	Trend of the silane & heat treated fibre mat in ACNT matrix composites for tensile and flexural modulus (decreasing order)	157
Table 4.3:	Tensile and flexural properties of amino silane treated GF in different epoxy matrix compositions	159
Table 4.4:	Tensile and flexural properties of epoxy silane treated GF in different epoxy matrix compositions	160
Table 4.5:	Comparison of the mechanical properties for ACNT/hardener GFRP composite	166
Table 4.6:	Summary of the improvement in mechanical properties for ACNT ASGFRP composite (amine-rich resin system)	169
Table 5.1:	Key parameters of hygrothermal study	172
Table 5.2 :	Concentration of salts in simulated sea-water	176-177
Table 5.3:	Types of samples tested for different hygrothermal aging conditions	179
Table 5.4 :	Equilibrium water content and diffusion coefficients for different	185

GFRP composites and hygrothermal conditioning

Table 5.5:	Summary of change in mechanical properties of PCNT GFRP composites after 2904h (121 days) of aging in SW and DW	199
Table 5.6:	Summary of the mechanical properties of EP GFRP samples after hygrothermal conditioning in DW for 121 days	205
Table 5.7:	Mechanical behavior of ACNT GFRP samples after immersion in SW at 55°C	219
Table 5.8:	Mechanical behavior of EP ASGFRP samples after immersion in SW at 55°C	219
Table 6.1:	Nomenclature for manufacturing defects and in-service damages in EP GFRP composite sheet	239

Chapter 1. Introduction

1.1 GFRP composites

The present technology requires hybrid materials which possess multifunctional properties that cannot be obtained by conventional metal alloys, steel, aluminum, ceramics and polymeric materials when used individually. On commercial ground, this necessity led to the invention of ‘composite’ materials in the late 1940’s and are the most advanced and adaptable engineering materials since then. A composite is a combination of two or more materials that provide the most desirable and unique physical and mechanical properties of its constituents, while suppressing their least desirable properties. Additionally, these materials possess excellent flexibility as they can be tailored according to the customer requirements by varying their components, proportions, distributions, morphologies, degree of crystallinity, structure and composition of the interface between components etc. Besides man-made materials, composites do occur in nature as well. For example, in tree trunks, spider webs, and mollusk shells, etc. A tree is a natural composite as it consists of cellulose (the fibrous material) and lignin (a natural polymer) which forms the woody cell walls and the cementing (reinforcing) material between them.

With respect to modern materials engineering, a composite refers to a ‘matrix’ material that is reinforced with fibres. The matrix may be either metallic/ceramic or polymeric in nature. It gives the composites, their shape, surface appearance, environmental tolerance and overall durability. Few of the polymer matrices (thermoset or thermoplastics) commonly used in preparing fibre-reinforced polymer (FRP) composites are epoxy, vinyl ester or unsaturated polyester [Lata (2000); Jin *et al.*, 2011]. Amongst the various thermoset resins, epoxy has been widely preferred for manufacturing advanced composites due to its high availability, easier processing methods, stability, superior thermal and mechanical properties, chemical resistance and good price-to-performance ratio [Dalina *et al.*, 2014]. Further, the matrix tends to bind and hold the fibres intact during extreme loading conditions. Subsequently, the fibres act as a primary reinforcement in composite materials with the capability of handling excessive stresses while being partially pulled out during the deformation. As a result, it provides the composite material its macroscopic stiffness and strength properties. Hence, it is essential to choose an appropriate

fibre during the design and preparation of a composite. There are several types of commercial fibres such as glass, carbon or aramid fibres, but their use depends primarily upon its structural application and need of the industry. Interestingly, the most widely preferred reinforcement material for structural purposes in the transportation industry with the thermoset polymers, specifically epoxy resin, are glass fibres, due to their easier availability, processing, reliability and low cost. Glass Fibre-Reinforced Polymer (GFRP) composites contain two types of fibres namely: E and S-glass, where the latter is chemically inert; stronger, expensive and specifically used in the aerospace industry. On the other hand, E-glass available in the form of a chopped strand mat or woven fabric is considered as primary reinforcing fibre owing to its bulk production, high strength and stiffness along with a smooth surface finish at a significantly lower cost as compared to S-glass. There are several types of E-glass fibres, but amongst them Advantex® fibre has found huge commercial importance due to its boron and fluorine free chemical composition and significantly smaller environmental footprint as compared to other E-glass fibres. Additionally, these fibres possess excellent corrosion resistance in any liquid or wet environment, including water, acidic or weakly alkaline solutions and thus reduce the risk of catastrophic failure on exposure to harsh environmental conditions that is why these fibres hold a strong rationale for preparing naval structures.

Stimulated by the unique properties/characteristics of the constituents of GFRPs, several marine components such as ship hulls, bulkheads, decks, propellers replaced the conventional metal structures. Few main advantages of implementing GFRPs over traditional steel/aluminium structures in warships and submarines are: high strength-to-weight ratio, lower initial and maintenance costs and excellent corrosion as well as thermal resistance. Additionally, these materials, improved the stability, payload, apart from reducing the maintenance and fuel consumption costs [Ray 2005]. Recently, these strong, stiff, lightweight materials saw an increased use in the rehabilitation, repair, and retrofit of civil infrastructures for instance, replacement of bridge decks and wrapping for concrete columns.

The most common form of GFRP composite that gained industrial importance are laminates in which, several fibre layers are bonded together using a polymer resin under controlled conditions. However, the variations in the fibre orientation in each layer as well as the stacking sequence of the layers in a composite laminate results into wide range of physical and

mechanical properties. The various methods of manufacturing laminate composites are: hand lay-up, spray lay-up, autoclave, pultrusion operation, resin transfer molding (RTM), and vacuum assisted resin infusion molding (VARIM) technique which has been implemented in this research study [Chow *et al.*, 2015]. The advanced and newly developed VARIM technique has recently gained wide commercial acceptance due to its significant cost reduction for fabricating FRP composites vis-à-vis composites prepared using prepreg technology, which requires autoclave during the curing process and thus, adds an additional cost to the manufacturer. The shape and thickness of the composite material depend upon its application requirement.

Further, the industrial application of GFRP composites is primarily decided by its mechanical performance that in-turn depends upon the fibre-matrix interface. The fibre-matrix interface is further related to the strong bonding between the epoxy matrix and the glass fibres. During loading conditions, this interface acts as an intermediate bridge that tends to transfer the mechanical stress from the matrix to the reinforcing fibres through the shear flow. Hence, it is an essential design parameter that controls the strength and stiffness of the composite material.

In order to further enhance the strength and stiffness of GFRPs for various industrial applications, micro-fillers were incorporated into the surrounding matrix. In order, to achieve the desired properties of the structural components, high loading of fillers was required, which further led to an increase in weight and a poor aesthetic look of the component. It then became essential to develop composite materials which were light weight, possessed high strength-to-weight ratio and also economical for manufacturing. Thus, the focus of research in materials engineering shifted from incorporating micro-fillers to nano-fillers. Subsequently, the field of nanotechnology had shown exponential advancement in various fields, specifically in inventing different types of nano-fillers and their interaction with the matrix. These findings were implemented to develop nanomaterials, where the polymer matrix was reinforced with nano-fillers and such composites were referred to as Polymer nanocomposites (PNC). A common practice was to disperse nanoparticles into the polymer matrix during the processing phase by weight percentage (wt%) (called mass fraction), in the range of 0.5– 5%. Pilot studies revealed that significantly lower loading of nano-fillers was sufficient to obtain composites with desired properties. The nanocomposites fabricated at loading levels of 2-3 wt% offered similar or better mechanical performance as that of conventional composites with 30-50 wt% of micro-fillers

[Utracki & Kamal 2002]. Furthermore, there was a significant weight reduction due to lower filler loading and drop in total cost of the nanomaterials because of the lower amount of filler used. Consequently, nano-fillers were incorporated for preparing important military and aerospace structural components.

The possible reasons that support their vast applications is the exceptionally high surface area-to-volume ratio of the reinforcing phase and high aspect ratio (length: diameter ratio) of the nano-fillers. This ratio implies that for the same particle loading, nanoparticles had a much greater interfacial area than micro-particles as illustrated schematically in Figure 1.1, which eventually affects the material properties to a greater extent. The mechanical benefits of PNC over conventional composites are: enhanced strength of composites due to the strong adhesion of nanoparticles with the polymer matrix, increase in the strength of the nanocomposites due to the presence of small nano-fillers in the empty spaces of the matrix that allows nanoparticles to form stronger interfacial bonds with the surrounding particles of the matrix or the glass fibres. Hence, the unique and intrinsic properties of the nanoparticles such as size in nanoscale, high specific surface area (SSA) and the possibility of chemical interaction with the conventional reinforcements led to an extensive research and development in the area of polymer nanocomposites.

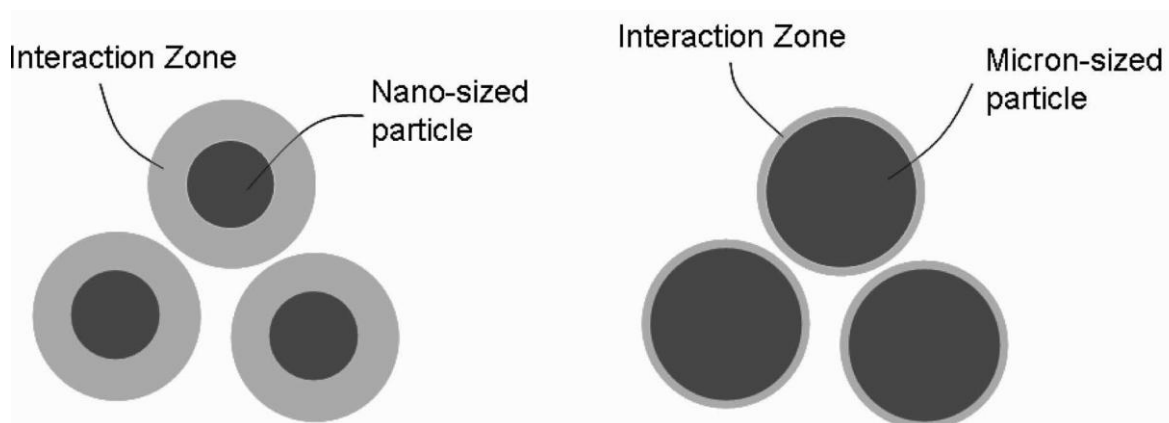


Figure 1.1: A schematic diagram that compares the particle and matrix interaction in nanocomposites and micro-composites [Source: Li Y *et al.*, 2010]

In brief, extensive research has shown that the nanocomposites encompass unique chemical, physical, mechanical, thermal, electrical and optical and biological properties which make them an ideal candidate for electronic, medical, advanced structure, energy and

transportation industries. For the purpose of developing hybrid material system, the researchers incorporated nano-fillers such as Carbon nanotubes (CNTs), carbon nanofibers, nanoclays in epoxy matrices and reported enhanced mechanical properties and durability [Young and Jae 2005, Fiedler *et al.*, 2006, Baljinder *et al.*, 2010, Chua *et al.*, 2010].

1.2 CNT modified GFRP composites

Amongst the various nano-fillers CNTs have drawn specific interest as structural reinforcement since its discovery by S. Iijima in 1991 [Iijima 1991] for both research and preparing advanced composite structures as compared to other fillers owing to their unique properties and length: diameter ratio. In addition to their low density ($1.3 - 2 \text{ g/cm}^3$) and high aspect ratio (1000s), CNTs have outstanding mechanical properties such as strength (10 – 60 GPa), which is 10-100 times that of steel and stiffness (1 TPa) close to that of diamond. Additionally, their electrical conductivity ($10^6 - 10^7 \text{ S/m}$) is approximately 1000 times that of copper and thermal conductivity ($> 3000 \text{ W/m.k}$) about twice as high as diamond along with stability up to 2800°C in vacuum conditions. As a result of such unique combination of physical and multifunctional properties, CNTs have become a strong candidate for use as tailoring agents in various polymer matrices in order to develop the next generation multiphase composite materials [Ajayan *et al.*, 1994, Sandler *et al.*, 1999, Min-Feng Yu *et al.*, 2000, Bekyarova *et al.*, 2007 (a, b), Li and Chou 2009, Ma *et al.*, 2010]. It is worthy to mention that CNTs till date have been incorporated in developing various industrial applications such as space shuttle components, tennis rackets, lens cleaners, bicycles, water-filtration systems, automotive components and also used as drug delivery agents. Recently, CNTs were introduced in cement to prevent crack growth, enhance mechanical strength and also to provide real-time structural health monitoring due to their good conductivity and damage sensing properties. It appears that the structure of the nanotube is the predominant parameter influencing the properties and application of nanotubes in real-world.

In general, the structure of CNTs on visualization under the electron microscope, reveals a thin sheet of graphene rolled into a tubular structure. The atomic arrangement and the morphology, or nano-structure of these rolled graphene sheets are the backbone of its superior properties. Researchers have found that CNTs exist in many structures due to the variation in length, thickness and in the type of helicity and number of layers. Three commonly seen CNT

structures are: Single Walled Carbon Nanotubes (SWCNT), Multi Walled Carbon Nanotubes (MWCNT) and Double Walled Carbon Nanotubes (DWCNT) as illustrated in Figure 1.2a, 1.2b and 1.2c, respectively. SWCNT are hollow cylinders composed of a carbon hexagon pattern replicated through the entire structure. These are mechanically stronger, electrically and thermally more conductive, and chemically more active than graphite. In terms of applications, it is widely used as support materials for electro-catalytic applications like fuel cells. They have been used scarcely as a reinforcement material for both mechanical and thermal applications, possibly due to their surface interactions ($SSA > 1000 \text{ m}^2/\text{g}$) which results in the formation of huge sized carbon agglomerates appearing as ropes or bundles and act as damage sites. However, the synthesis of SWCNT is a very complex process that eventually lowers its productivity and increases the cost of production.

On the other hand, MWCNTs are a group of co-axially situated SWCNTs of different radii that are often capped at both ends. The range of diameter varies from a few nanometers (nm) to 200 nm. These concentric nanotubes are held together by strong van der Waals forces. Interestingly, MWCNTs are widely preferred both for academic and industrial purposes due to its lower SSA ($200 \text{ m}^2/\text{g}$) which further minimizes the carbon attractions and results in less chance of agglomerations, easier manufacturing, ease of dispersion, greater availability and low cost, as compared to SWCNT. Figure 1.3 is a Transmission Electron Microscope (TEM) image depicting the multi-layers of graphene carbon along with a hollow core for a MWCNT.

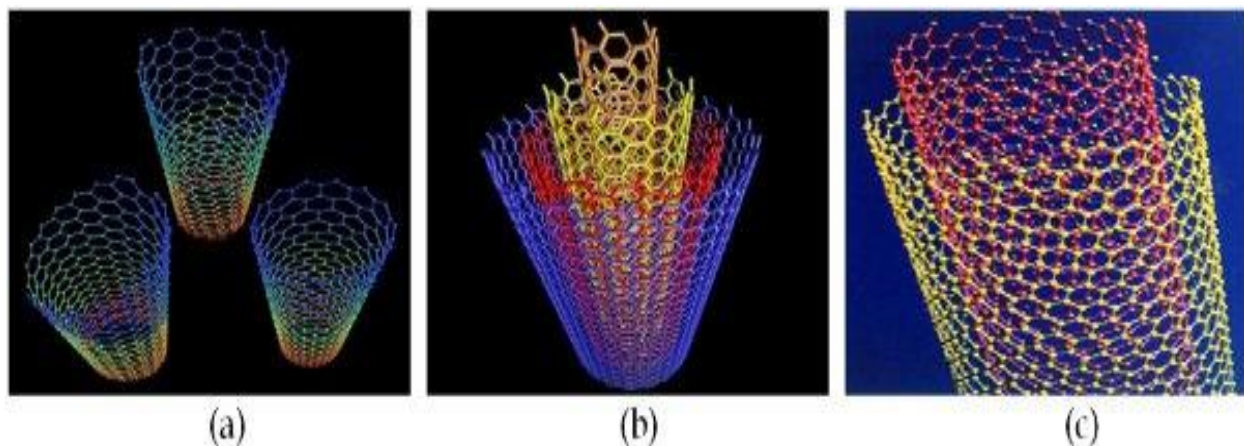


Figure 1.2: Three different types of carbon nanotubes a) single walled b) multi-walled c) double walled. [Source: Harris, (1999)]

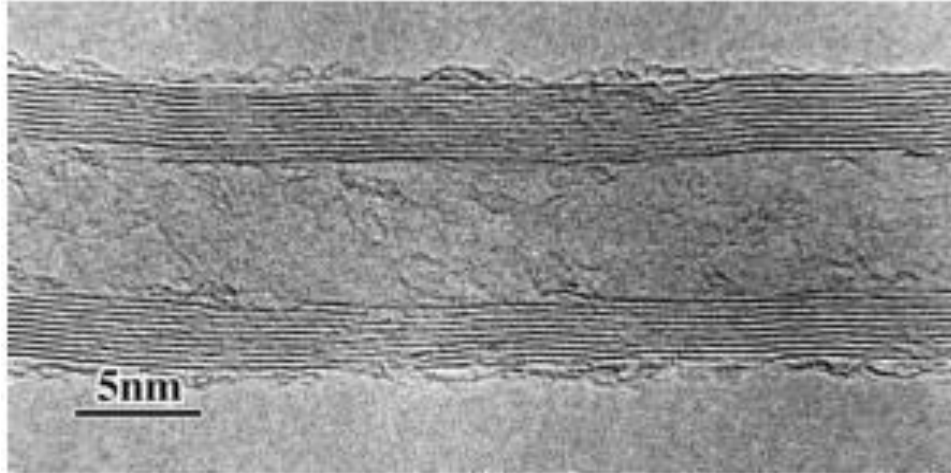


Figure 1.3: TEM image showing the structure of a MWCNT

The main motivation for using CNTs as reinforcement in FRP composites is to alleviate the existing limitations associated with poor interfacial bonding between the fibres and polymer matrix during stress conditions. The two widely used methods for effectively exploiting the superior properties of CNTs are: (i) by uniformly dispersing nanotubes throughout the composite (epoxy) matrix, (ii) grafting the nanotubes directly onto the surface of glass or carbon fibres. Scientists have reported that, the grafting technique introduces functional groups at the interface of the final composites thus increasing the interfacial strength, possibly due to stronger chemical bonding and mechanical interlocking at the fibre-matrix interface [Zhang *et al.*, 2010, Gao *et al.*, 2010, 2011]. Additionally, it also lessens the problem of CNT agglomeration and incorporation of higher CNT content. But to practically implement the grafting methodology, it requires an advanced process development, both for the initial synthesis and consequent preparation of advanced composites. In addition, few researchers have also reported that the catalyst reactions of CNTs damage the primary fibres and reduce their tensile strength by approximately 15-55% for both carbon [Qian *et al.*, 2008, 2010a, Zhang *et al.*, 2009, Sager *et al.*, 2009] and glass [Qian *et al.*, 2010b] fibres. Due to the potential damage to the fibres during CNT grafting and the difficulty of controlling the uniformity of the grafted CNTs, the other method i.e. uniformly dispersing CNTs in the epoxy matrix is more preferable and the same has been investigated in this study, particularly for glass fibres.

In order to fully utilize multifunctional properties of CNTs as reinforcing agent in the polymer matrix, particle-particle and particle-matrix interaction plays a vital role and amongst

various dispersion methodologies, *in-situ* polymerization has been considered to be highly effective [Park C *et al.*, 2002, Fiedler *et al.*, 2006, Yeh *et al.*, 2008, Chakrabortya *et al.*, 2012, Goyal *et al.*, 2015]. Specifically, the strong particle-matrix bonding allows the stress to be transferred from the matrix to the nanotubes during loading conditions, which ultimately improves the mechanical performance of the nanocomposites. The *in-situ* methodology has the advantage of simplicity and compatibility with widely available industrial equipments such as shear-mixing and sonication. From a mechanical perspective, the design of a strong fibre-matrix interface is the most important and challenging task. The presence of a strong interface allows the efficient transfer of stress from the matrix to the fibres during loading conditions. The interface is further strengthened by homogeneously dispersing CNTs in the polymer matrix as CNTs assist in further increasing the load bearing capacity of the matrix itself. However, despite immense efforts the potential of utilizing the properties of the nanotubes embedded in a polymer matrix still remains a key challenge. A primary difficulty is to achieve a uniform and homogenous dispersion of the nanotubes in a matrix and build strong interfacial adhesion between CNTs and the polymer matrix, which is one of the primary goals of this research project. Explicit studies by various groups around the globe have reported that <1.0 wt% CNT loading in matrix shows uniform and homogenous dispersion while, a further increase causes the formation of CNT agglomerates. The primary reason for agglomeration is that the CNTs tend to attract each other due to the presence of weak van der Waals forces and Coulomb attractions even in an uncured polymer matrix [Bryning *et al.*, 2005, Li J *et al.*, 2007]. Additionally, the high aspect ratio of CNTs and strong forces of attraction between the carbon particles are also a factor for agglomeration. These further influences the homogeneous dispersion and interfacial bonding thus, affecting the material properties. Hence, it is clear that the interfacial bonding between the composite constituents is a critical parameter that needs to be considered during design as it controls the mechanical performance of the resulting polymer composites [Kim and Mai 1991, Kim and Mai 1993]. Thus, the presence of strong covalent bonding between the CNTs, epoxy matrix and the fibres is a primary step to observe an improvement in mechanical behavior of CNT GFRP composites.

However, to develop such advanced composites with improved covalent bonding and uniform dispersion of nanotubes in polymer matrix (for example epoxy, vinyl-ester etc.) different processing techniques such as calendaring [Gojny and Schulte 2004a, Thostenson and Chou

2006, Seyhan *et al.*, 2007, Thostenson *et al.*, 2009], ultrasonication [Gojny and Schulte 2004a, Shen *et al.*, 2007a] and high-shear mixing [Sandler *et al.*, 1999, Gojny *et al.*, 2003] have been practiced by various researchers. But, no standard procedure or protocol has been established or reported for achieving homogeneous dispersion and good interfacial bonding between the CNTs and the polymer matrix.

On the other hand, epoxy nanocomposites that incorporated pristine or non-functionalized nanotubes (PCNT) as a secondary reinforcing agent [Sandler *et al.*, 1999, Kinloch *et al.*, 2002, Song and Yuon 2005, Huang *et al.*, 2006, Rahatekar *et al.*, 2006, Kovacs *et al.*, 2007, Chandrasekaran *et al.*, 2011] reported insignificant improvement in properties likely due to poor dispersion and weak bonding of PCNTs with the epoxy resin. However, chemical functionalization of the nanotubes such as amino functionalized nanotubes (ACNT) led to better dispersion than PCNT in the polymer matrix. It also helped in forming strong covalent and ionic bonds with the epoxy matrix that enabled a more effective transfer of stress between the epoxy matrix and CNTs along-with an improvement in interfacial adhesion [Gojny *et al.*, 2003, Titus *et al.*, 2006]. In general, the chemical functionalization of CNTs introduces carboxylic groups (-COOH) on its surface, which is further chemically treated to attach functional groups such as chlorine, amine and silane on the surface, depending upon its application. Abundant literature and observations support the fact that free amino groups on the surface of CNTs react with the polymer molecules during the curing stage, develop equivalent bonds, leading to an improved nanotube matrix bonding, enhancement in mechanical performance and modifies the curing mechanism as well as the glass transition temperature [Gojny *et al.*, 2003, Gojny and Schulte 2004a, Wang J.G. *et al.*, 2006, Shen *et al.*, 2007a, Ma *et al.*, 2010, Chandrasekaran *et al.*, 2011, Rahman *et al.*, 2012, Garg *et al.*, 2015].

From the above discussion, it is clear that the performance of PNC is a function of the interfacial properties, which is governed by the load transfer capability between its major components i.e. matrix and fibre surface during mechanical loading conditions. So far, it has been witnessed that the incorporation of nanotubes into the epoxy matrix enhanced the interfacial bonding and stress-transfer mechanism from the ‘weak matrix’ to the ‘strong nanotubes’. Therefore, the principle of interfacial adhesion observed at the nanoscale must also be true for macro-level reinforcement. For the purpose of enhancing mechanical behavior and to strengthen

fibre-matrix interface, glass fibres are commonly treated with organosilanes/silane coupling agents. A strong interfacial bonding is expected to improve the composite's shear, compressive and off-axis strengths.

1.3 Silane treatment of glass fibres

In 1940's when FRP composites were first prepared, their strength was higher than other conventional materials but started to decline after aging in underwater. This was due to the weakening of interfacial bond strength between the fibres and the resin. Researchers then investigated this in depth and came with a solution that, the bonding between the fibres and the resin can be improved by exposing the commercial glass/carbon fibres to various types of treatment such as exposure to high temperature and/or by using chemical agents that replaces the commercial fibre sizing with an active functional group on its surface [Callister 2001, Beg and Pickering 2006, Xie *et al.*, 2010, Isa *et al.*, 2014, Mahjouba *et al.*, 2014, Punyamurthy *et al.*, 2014, Tzounis *et al.*, 2014, Fiorea *et al.*, 2015, Ku-Herrera *et al.*, 2015, Nattapat *et al.*, 2015, Parida *et al.*, 2015]. Following this methodology, the active polar groups (from the organosilanes) are introduced onto the fibre surface in a manner that they chemically interact with the resin (for e.g. amino silane groups react with epoxy resins).

The organo-functional silanes referred to as silane coupling agents, consist of molecules that carry two different reactive groups on a silicon (Si) atom so that they can react and form different types of bonds simultaneously with different materials (for example, inorganic surface and organic resins) as shown in Figure 1.4. It is reported that there exists three different types of bonding between the coupling agents and the matrix: chemical bonding, hydrogen bonding and interpenetrating polymer network. Among these, chemical bonding is the most important and vital factor that improves the interfacial strength and mechanical properties of the FRP composites. Also, silanes has been recognized as an efficient coupling agent due to their bridging mechanism and used extensively in composites as well as for adhesive formulations. They have also been implemented in GFRPs and mineral filled polymer composites [Clark and Plueddemann 1963, Wu H.F. *et al.*, 1997, Favis *et al.*, 2003].

Figure 1.4 illustrates the basic structure of a silane coupling agent. The silane coupling agents consist of one organic and three hydrolyzable substituents. As clearly visible in Figure

1.4, the silane agent shows two classes of functionality. X is a hydrolyzable group typically alkoxy, acyloxy, halogen or amine. Following hydrolysis reaction, a reactive silanols group is formed, that either forms a siloxane bond with the inorganic material or might condense with other silanols groups. Whereas, R is a nonhydrolyzable organic radical that will react with the organic material to form a covalent bond between the polymer resin and the fibre surface. Most widely used functionalities of silane agents are: amino, mercapto, glycidoxo, vinyl, or methacryloxy groups. Amongst these different silane functionalities: aminosilanes and glycidoxysilanes, specifically 3-aminopropyltriethoxysilane and 3-Glycidyloxypropyltrimethoxy, are widely used as coupling agents [Park *et al.*, 2000, Zinck *et al.*, 2001, Shokoohi *et al.*, 2008, Xie *et al.*, 2010, Tzounis *et al.*, 2014]. In order to fully utilize the silane agents for developing stronger interfacial bonding, it is essential to understand their step-by-step hydrolysis process as illustrated in Figure 1.5.

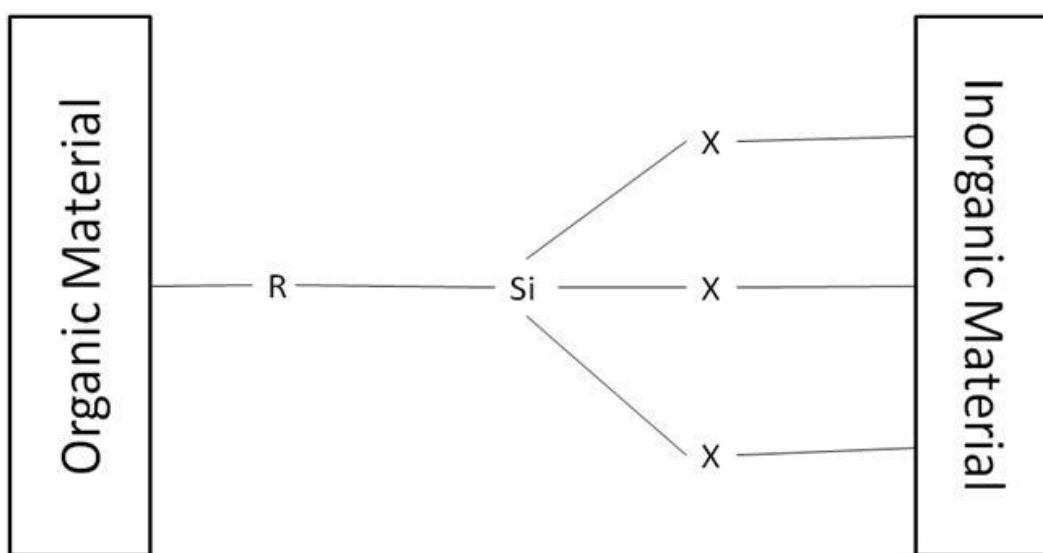
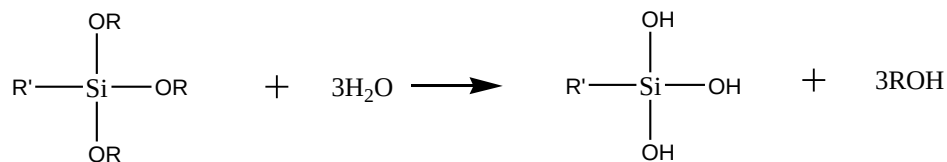


Figure 1.4: Schematic representation of silane coupling agents

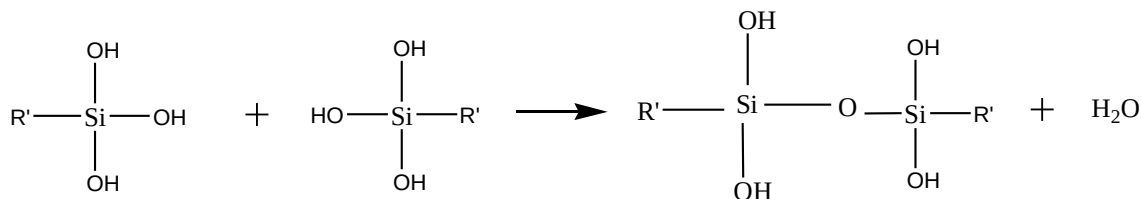
The reaction of silane with the fibre surface is divided into four steps. Firstly, Si-OR bonds hydrolyze readily with water, or the moisture absorbed from the air, to form Si-OH groups. It is then followed by condensation reaction during which, the silanol groups, possibly condense with each other to form a stable polymer structure with Si-O-Si bonds as shown in Figure 1.5. Further, they condense with hydroxyl groups on the fibre surface to form stable bonds with the inorganic glass fibre. Lastly, during the drying stage either at room or higher

temperature, it results in surface treatment and coupling facilitated by strong covalent bonds between inorganic fibres and organic resin, which continues to follow a cross-linked polymer chain along with the related loss of water.

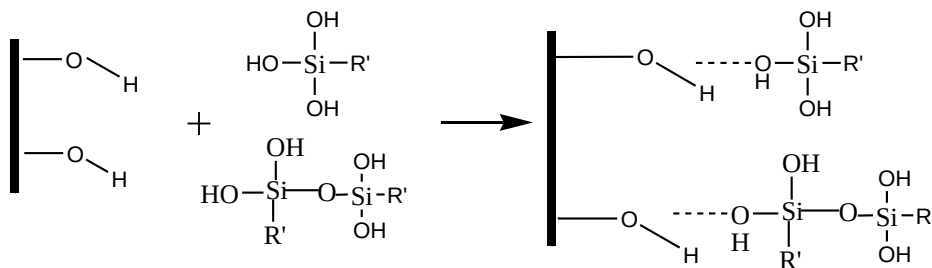
(a) Hydrolysis:



(b) Self-condensation:



(c) Adsorption:



(d) Bond formation:

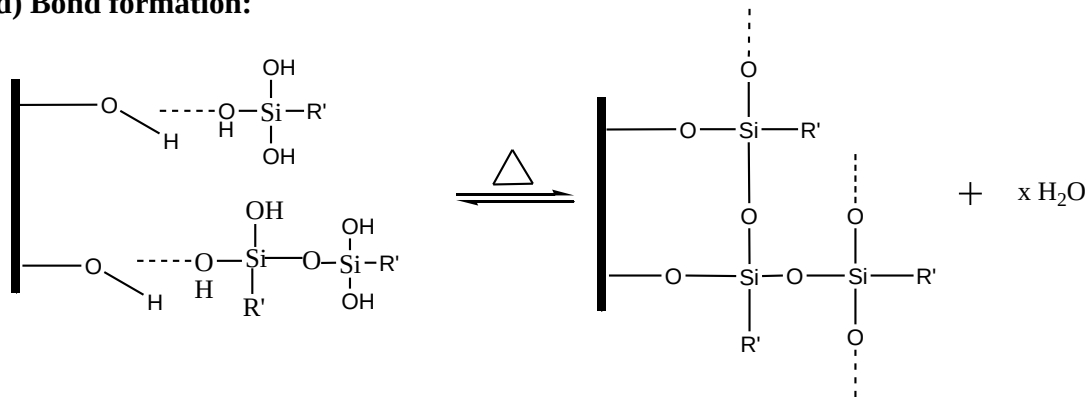


Figure 1.5: Hydrolysis process of silane coupling agents [Source: Zhao *et al.*, 2012]

From the hydrolysis process it is evident that if a proper silanization procedure is followed, it will form strong and stable covalent bond between the inorganic glass fibre surface and the organic epoxy resin matrix. Despite effective bonding, silane agents also act as a lubricant and protect the wet strands of fibre against friction and breakage. Hence, the strong and stable interfacial adhesion with the epoxy resin and enhanced mechanical properties of silane treated GFRP composites depends mainly on: the type and quantity of the silane agent used. Literature has stated another important benefit of a thin silane layer on glass fibre i.e. improved resistance during exposure to harsh environments, such as prolonged hygrothermal conditions and thermal cycling [Pantano and Wittberg 1990, Noobut and Koenig 1999, Kim *et al.*, 2001, Brill and Palmese 2006].

Therefore, the stiffness, strength, elongation at break and longevity are some of the key parameters that need to be quantified for GFRP composites. This can only be reported after exposing the prepared advanced composite materials to actual in-service conditions. For that purpose, a comparative analysis has been carried out between hygrothermally aged and unaged specimens, the same have been discussed ahead.

1.4 Hygrothermal aging

Hygrothermal refers to those environmental conditions where a material is exposed to varying moisture, water and/or temperature conditions. Initially, steels were used in building naval structures such as boats, submarines and ships for centuries, but it emerged as a serious issue worldwide with respect to the short-life of ships and significant maintenance costs. The steel corroded in a short span and exhibited degradation in strength and stiffness on exposure to different seawater conditions. In order to overcome such issues and considering the global perspective of naval structures, a remedy in the form of anti-corrosion coating was implemented on various parts of the ships to increase the life span of the ship. However, the results were not satisfactory and it led to the implementation of FRP composites in manufacturing various ship components. In 1940, the use of FRP for naval application was driven due to their easy fabrication, being lightweight, strong, corrosion resistant, eco-friendly having high durability, low thermal conductivity, and lesser maintenance costs as compared to conventional materials like aluminum alloys and various types of steel etc. [Gellert and Turkey 1999, Ray 2005, Kar *et al.*, 2008, Chakraverty *et al.*, 2015]. But, as the hygrothermal aging time increased, absorption of

water and/or moisture also followed the same trend and affected the mechanical behavior of the composites. Amongst several polymer composite materials, Glass/epoxy (referred to as EP GFRP in this study) and glass/polyurethane are widely used for manufacturing various marine structural components. The exposure of glass or carbon fibre/epoxy composites to humidity, water, elevated temperatures, thermal spiking, and other harsh seawater environment for years together have shown both physical and chemical changes in the composites [Surathi and Karbhari 2006, Chakraverty *et al.*, 2013, José *et al.*, 2016]. In view of the water exposure, for the past two decades the researchers have tried to determine the effect of different GFRP composites when immersed in different types of water (seawater, distilled water, tap water, etc.) with respect to their durability and performance.

The findings by Wood and Ellyin [Wood and Bradley 1997, Ellyin and Rohrbacher 2000] have reported that the absorption of distilled water and/or seawater in GFRP composites causes changes in the thermophysical, mechanical and chemical characteristics of the epoxy matrix due to plasticization, hygro-strains and hydrolysis. Generally, when FRP composites are submerged in water, it fills the gap between the polymer molecules and reduces its glass transition temperature (T_g). This results in lowering the modulus and strength of the composites. While the modulus decreases, the ultimate strain increases, which suggests the plasticizing effect of the polymer on being exposed to water/moisture for longer durations. Additionally, excess water absorption into the matrix results in its expansion, which tends to damage the strong fibre-matrix interfacial adhesion and builds hygro-strains in the composite that eventually, lowers the resistance of the material to the surrounding factors. From the experimental and simulation hygrothermal studies, it has been analyzed that epoxy systems have more affinity for water/moisture absorption. The water primarily enters into the matrix followed by the fibre-matrix interface and lastly inside the fibres. Subsequently, it leads to a progressive decline in the material properties such as compressive strength, inter-laminar shear strength, fatigue resistance and impact strength [Wong and Broutman 1985, Chin *et al.*, 1997, Brondsted *et al.*, 2005, Segovia *et al.*, 2007, Aldajah *et al.*, 2009]. The composite materials used in marine application are generally exposed to different temperatures in sea water.

Another important factor that affects the material degradation is the temperature of the hygrothermal environment. For example, the ship experience temperature variation during their

sail and this varies from location to location. Research has attempted to differentiate the effect of aging GFRPs at an ambient temperature as compared to a higher temperature. At room temperature, swelling and plasticization led to a relaxation of curing stresses thus, compensating for any interfacial degradation that might have been caused due to moisture. Whereas, exposure at higher temperatures leads to an increase in moisture absorption but, tensile strength, ductility [Wood and Bradley 1997] and interfacial adhesion of the composite decreases. Therefore, from the above mentioned literature, it is clear that the mechanical properties of aged GFRP materials plunge due to following mechanisms: interface degradation, matrix plasticization, hygro-strains and stress corrosion, which are seen to be a factor of the quantity of water absorbed into the composite. From the hygrothermal analysis, weak design issues were identified and attempts were made to overcome the problems faced. Interestingly, the design process has evolved with some major improvements in the last decade, but, it is still considered to be an ongoing endeavor due to its requirement of developing a strong, stable material that has the capability of reducing water intake, retain its properties and show minimal deterioration on exposure to varying hygrothermal conditions for longer durations [Chifu and Iroh 1996, Davies *et al.*, 2001, Aktas *et al.*, 2002 (a, b), Wu L. *et al.*, 2002, Kootsookos and Mouritz 2004, Mula *et al.*, 2006, Aldajah *et al.*, 2009, Chakraverty *et al.*, 2013, Chakraverty *et al.*, 2015].

Consequently, the exposure of GFRP components (used in marine structures) to environmental degradation and service related factors affect the fibre-matrix interfacial bonding, which introduces damages and deteriorates its structural performance. The common damage behavior exhibited by FRP components under harsh service conditions includes transverse micro-cracking, fibre-breakage and delamination [Sihn *et al.*, 2007]. Hence, it is imperative to develop their real-time health monitoring methodology in a submerged state using an advanced technique which can replace the conventional methods of testing.

Thus an attempt has been made in this study to develop advanced glass fibre reinforced polymer composites by reinforcing epoxy matrix with nano-fillers and introducing active functional groups on the fibre surface. These composites were then subjected to tensile and flexural loading conditions to determine their behavior under dry conditions, i.e. without exposure to the water environment. This was then followed by investigating the hygrothermal performance of the fabricated composites for different conditions such as: types of water, aging

time, composition, effect of edge coating and lastly, temperature. Characterization techniques such as Scanning electron microscope (SEM) and Fourier-transform infrared spectrometer (FTIR) have been used periodically in this study to confirm the morphological and chemical changes in the composites. Further, the present study attempts to ultrasonically monitor defects encountered in GFRP laminates using a non-contact, mobile and real-time guided wave technique and the same has been discussed in the next section.

1.5 Damage monitoring in GFRP laminates

Nowadays, since the GFRP composites are replacing conventional steel/aluminum (or their alloys) for naval structures the damages encountered are mostly transverse micro-cracking, fibre-breakage and delamination. Initially, the ply failure begins with transverse micro-cracking through its thickness followed by delamination and lastly by fibre breakage. Growth and propagation of such damages in composites is very complex and depends on various factors such as constituent materials, fibre orientation, stacking sequence, exposure conditions etc. (Sihn *et al.* 2007). In addition to service induced damages some defects may be inherently present in GFRP composites during the manufacturing phase. Commonly observed manufacturing defects include air gaps, debonding, and non-uniformity of the matrix. The presence of such defects in FRPs reduces their performance and durability.

Hence, it became essential to monitor the health of the material as a continuous process such that preventive actions could be taken well in advance of the complete failure. With this objective, researchers developed several non-destructive techniques (NDT) specifically, for composite materials. Techniques such as thermography [Bates *et al.* 2000, Chaki *et al.* 2015, Palumbo *et al.* 2016], acoustography [Chen *et al.* 2001, Chaki *et al.* 2015], laser ultrasonics [Scudder *et al.* 1996, Ann *et al.* 2005, Rizzo *et al.* 2010, Pistone *et al.* 2013, Hong *et al.* 2015, Harb and Yuan 2016], and shearography [Hung *et al.* 2000, Okafor *et al.* 2001, De Angelis *et al.* 2012, 2015] have been proposed by various researchers for damage detection in composites. However, for naval applications, the regular assessment of composites in submerged condition is inhibited by the conventional damage inspection tools due to economic constraints such as high out-of-service cost linked with frequent monitoring schedules and also time consuming process associated with the removal of structures prior to their inspection. As a result, it exposes such structures to the risk of unnoticed fatal damages with huge loss of human life and property. To

detect damages such as air gaps, effect of missing epoxy, fibre breakage, delamination, cracks, etc. in GFRPs, ultrasonic guided waves have been suggested as an effective structural health monitoring tool by various researchers [Datta and Kishore 1996, Badcock and Birt 2000, Kessler *et al.* 2002, Toyama *et al.* 2003, Kim Young-Han *et al.* 2007, Benammar *et al.* 2008, Miao *et al.* 2012, Ben *et al.* 2014, Providakis *et al.* 2014, Wada *et al.* 2015, Putkis *et al.* 2016].

Guided waves exploit the geometrical boundary (e.g. tube, cylinder or plates, etc.) of the structure as a guiding surface for wave propagation. In the structures with a plate or sheet geometry, guided waves are called Lamb waves. These are complex vibrational waves that propagate parallel to the surface throughout the thickness, thus scanning the entire thickness of the plate. Propagation characteristics are dependent upon the density, elastic properties, geometry of the structure and frequency of excitation. As compared to ultrasonic bulk waves the Lamb waves are characterized by longer propagation, lower attenuation, economical implementation, high sensitivity to structural damages and to the material in-homogeneities, ease of generation and acquisition of signals [Wilcox *et al.*, 1999, Na and Kundu 2002]. Owing to these characteristics, Lamb waves have been widely used by various researchers for damage detection in FRPs [Badcock and Birt 2000, Pavlakovic *et al.* 2001, Diamanti *et al.* 2002, Kessler *et al.* 2002, Worden *et al.* 2003, He *et al.* 2006, Kim Young-Han *et al.* 2007, Ratnam *et al.* 2008, Ramadas *et al.* 2011a, Liu *et al.* 2012, Moll *et al.* 2012, Providakis *et al.* 2014, Harb and Yuan 2016].

In most of the reported work, contact probes have been used to generate guided waves. The key obstacles in implementing contact transducers are: inadvertent variations in contact pressure affecting the repeatability of results, difficulty in generating specific Lamb wave mode, and finally the possibility of local damage due to use of contact probes. Few studies have attempted to generate Lamb waves in FRP composites by using either air-coupled [Castaings and Hosten 2001, Ann *et al.* 2005, Ramadas *et al.* 2011b, Liu *et al.* 2013, Chakrapani and Dayal 2014, Harb and Yuan 2016] or fluid coupled [Ghosh *et al.* 1998, Ben *et al.* 2013] non-contact ultrasonic transducers. The use of air/fluid coupling ultrasonic transducers also has several limitations such as: difference in mechanical impedance between air/fluid and the sample under investigation resulting in low precision, removal of the structure from its service conditions in order to access the structure from both the sides and relatively less-effective technique for

detecting near-surface damages. Another group of researchers [Rizzo *et al.* 2010, Pistone *et al.* 2013, Rizzo *et al.* 2015, Pistone and Rizzo 2015, Bagheri and Rizzo 2016] used laser ultrasonics to fine tune the incident angle and exploit specific Lamb wave mode to detect damage in submerged steel plates and underwater pipes. Recently, Sharma and Mukherjee [2014, 2015 a, b] developed a real-time non-contact damage monitoring methodology for submerged steel plates using specific leaky Lamb waves. Initially, specific Lamb wave mode with the unique scanning capability were identified and excited by orienting the transducers at a particular angle and at appropriate distances. The drop in voltage amplitude was correlated to the extent of damage such as depth of the notch in the steel plate. Further, the developed methodology was able to pictorially represent the defect type and its extent in the form of tomograms. Besides this, the *in-situ* and non-contact Lamb wave mode were effective in monitoring progressive corrosion in steel plates and develop a relation with the mass loss, stress-strain behavior and tensile strength at each stage. Although considerable progress has been made in using Lamb waves for damage detection in various structural applications, but research on their use for health monitoring of FRPs laminates is limited.

In totality, the objective of the present work is reinforcement of EP GFRP composites at the nanoscale with carbon nanotubes and at the macro-scale with fibre treatment along with uniform dispersion and strong fibre-matrix interface, which makes it viable to study the role of such advanced composites in hygrothermal conditions. For the very first time applicability of CNT reinforced glass fibre composites on the diffusivity and material degradation is explored in context of seawater exposure in this research study. In addition, the present study proposes an effective damage monitoring methodology in GFRPs which is non-invasive, non-contact, and *in-situ*. The developed methodology has the capability to monitor both manufacturing defects and in-service degradation due to hygrothermal aging. This investigation also reports a relation between mechanical performance and guided wave parameters after monitoring the progressive aging effect in EP GFRP sheets.

1.6 Outline of thesis

The present study sheds light on mechanical performance, morphological characterization and hygrothermal response of GFRPs reinforced with functionalized and pristine carbon nanotubes prepared by *in-situ* polymerization. Further, the manufacturing defects or damages induced in the

composites due to usage or seawater exposure have been monitored using NDT technique and further correlated with the deteriorating tensile properties of the composite material.

This thesis embodies the subject matter resulting out of this study and is arranged in eight separate chapters. The outline of the chapters is listed below.

- **Chapter 1:** This chapter starts with the general introduction of polymer composites, its application and importance to the industry and converges to the need for developing nanocomposites and related dispersion and interfacial bonding effects of functionalized and pristine nanotubes in epoxy resin, as well as surface treatment of glass fibres. Further, hygrothermal aging is discussed, explaining the factors influencing different degradation mechanisms. Lastly, the significance and need for a non-invasive and *in-situ* damage monitoring technique for submerged FRP laminates is established by highlighting the drawbacks of the existing methods followed by an introduction to ultrasonic guided waves.
- **Chapter 2:** It provides a literature review incorporating the latest findings with respect to four major areas of this thesis, which are: (i) CNT modified glass fibre polymer composites, (ii) surface modification of glass fibres, (iii) hygrothermal aging of composites, and (iv) application of Ultrasonic guided waves for damage monitoring of composites.
- **Chapter 3:** It describes the methodology adopted to obtain uniform and homogeneous dispersion of nanotubes in epoxy resin. Further, it details the fabrication of nanocomposites using VARIM equipment. It also discusses the mechanical test result of fabricated GFRP composites in 0.0% CNT (neat epoxy), 0.1 wt% ACNT and 0.1 wt% PCNT compositions at stoichiometric ratio. The experimental results showed that the effect of utilization of intrinsic properties of CNTs in a multi-phase composite is a complex mechanism. In addition to this, samples were also prepared by modifying the epoxy: hardener ratio, specifically in amine-rich resin concentration. The relevant crosslinking reactions and morphological changes are studied and discussed in detail in this chapter. Furthermore, morphological and FTIR characterization techniques were adopted to cross check the interaction between CNT and epoxy resin along with their mechanical performance. Also, the study examined the effect of changing processing technique in order to disperse nanotubes in the polymer matrix. Furthermore, the effect of resin infusion temperature has also been investigated in the present study.

- **Chapter 4:** This chapter points out the rationale for choosing the two silane coupling agents, i.e. their possible interactions with the resin and the nano-fillers along with their chemical structures. Then the preparation of silane treated glass fibres along with the heat treatment effect has also been discussed thoroughly. To extend the complex crosslinking mechanism further, laminates of silane treated glass fibres reinforced with either ACNT or PCNT modified epoxy matrix were prepared followed by their mechanical and morphological analysis. Lastly, a composite with optimal nano and macro scale reinforcements was also prepared after incorporating the findings of the experimental study.
- **Chapter 5:** Firstly, it details about the various samples that were exposed to different hygrothermal conditions in order to evaluate the performance of fabricated composites with respect to its durability. Specifically, the study compares the exposure of EP GFRP, ACNT and PCNT GFRP samples in simulated seawater (SW) and distilled water (DW) conditions. In this chapter, the water uptake content and the diffusivity coefficient were determined from the diffusion study, followed by their mechanical tests and morphological analysis. Besides this, the effect of double edge coating versus single edge coating of the EP GFRP samples has also been looked into. Lastly, the samples (as stated above) were exposed to higher temperature and evaluated for mechanical and failure mechanisms after prolonged aging in SW.
- **Chapter 6:** In this chapter, a non-contact, *in-situ* and non-invasive technique for health monitoring of submerged EP GFRP laminates using ultrasonic guided waves has been proposed. Specific ultrasonic guided wave modes with good signal fidelity in the healthy EP GFRP prepared laminates were excited. The specific guided wave mode successfully picked up the manufacturing defects in EP GFRP such as air gaps and missing epoxy as well as were sensitive to degradation in the EP GFRP sheets due to its continual usage causing defects like notches/cracks, material degradation, surface discontinuities, etc. Quantitative evaluation of drop in transmitted ultrasonic signal strengths in defect ridden FRPs vis-à-vis healthy signal have been used to relate the extent of damage in FRPs. The methodology was also tested on the CNT GFRP laminate with different types of defects induced into the sheet. In addition, the damage detection methodology developed above was extended to EP GFRP samples undergoing hygrothermal aging in seawater environments. The degradation effect on

weakened fibre-matrix interface has been characterized and compared by performing tensile strength tests and guided wave signal strength in healthy and conditioned samples. The results obtained from this study using NDT provide a definite scope for further investigation of the sensitivity of Lamb waves in advanced nanocomposites and for specific defects.

- **Chapter 7:** In this chapter, the previously fabricated EP GFRP and ACNT GFRP samples were subjected to DSC analysis in order to study their degree of curing. The findings from the DSC analysis were incorporated to obtain a fully cured matrix by modifying the curing schedule. It was essential to carry out this study because the uncured polymer chains tend to attract and retain water molecules during exposure to moist conditions for e.g. in naval applications. Furthermore, different GFRP composites were manufactured as detailed in Chapter 3 and 4 by following the optimal curing schedule. Interestingly, the observations drawn from the results obtained in this chapter were consistent with our findings reported in earlier chapters.
- **Chapter 8:** It discusses the summary and significant findings of the experimental work of this thesis along with the scope for possible extension of the present work.

As per this outline, a thorough review of the literature is presented in the next chapter.

Chapter 2. Literature review

This chapter presents a brief overview of the literature stating the processing methods for manufacturing fibre reinforced polymer composites by introducing reinforcements at nanoscale and macro-scale. It is then followed by the hygrothermal behavior of composites on exposure to different environmental conditions. Lastly, it discusses about the application of Lamb waves for detecting different types of damages in plate-like structures, with more focus on composite materials.

2.1 CNT modified GFRP composites

This section presents a review of literature on the effect of using carbon nanotubes on the material properties in fibre reinforced polymer.

Salvetat *et al.*, (1999) reported about the mechanical properties of CNTs. High-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) techniques are used to determine the young's moduli of SWCNT bundles and MWCNT. The results from these techniques are confirming the theoretical predictions that carbon nanotubes have high strength plus extraordinary flexibility and resilience. They also concluded that composites will benefit from the exceptional mechanical properties of carbon nanotubes, but that the major outstanding problem of load transfer efficiency must be overcome before suitable engineering materials can be produced.

Gojny *et al.*, (2004a) investigated about mechanical properties of carbon nanotube- reinforced epoxy composites at low CNT content. A standard shear-mixing technique, calendaring is applied in order to disperse DWCNT in an epoxy resin. The prepared nanocomposites are investigated by transmission- and scanning-electron microscopy in order to obtain information concerning the dispersion and the CNT-epoxy interface. An addition of only small amounts of CNTs lead to improved mechanical properties like strength, stiffness, and fracture toughness.

Breuer and Sundararaj (2004) reviewed the recent studies on carbon nanotube/polymer composites. The tensile strength of CNTs is approximately 100-600 GPa i.e. two orders of magnitude higher than that of high strength carbon fibres, and the density of CNTs (1.3g/cm^3) are lower than carbon fibres ($1.8\text{-}1.9\text{ g/cm}^3$). The compressive strength of CNTs is two orders of

magnitude higher than any other fibre and also considered as one of the stiffest structures due to the high value of young's modulus (around 1TPa). The most remarkable effect, is the combination of high flexibility and strength with high stiffness which is not present in graphite fibres and makes CNTs as a remarkable reinforcing element. The strength of the nanocomposites prepared using CNTs depends on the two factors: high degree of load transfer between matrix and nanotubes, and the proper dispersion of the nanotubes in the matrix. The mechanical properties stated previously result in numerous applications of CNTs: aerospace structural panels, sporting goods, ultra-light, thin walled space structures for use in space, and high stiffness-to-weight property in space mirror substrates. Recently the CNTs have been used in automobile bumpers. The bumpers produced have good mechanical properties and are light-weight than the standard fibreglass bumpers, since only 1-5 wt% CNTs are needed in comparison to 30 wt% or more of fibreglass.

Shen *et al.*,(2007a) reported the synthesis of MWCNTs with different amino groups using chemical vapor deposition (CVD) process. The high surface area of the CNTs results in a high viscosity of the mixture and during the fabrication process it makes the dispersion of nanotubes difficult. In order to overcome this situation CNTs were functionalized with amino groups as they have high reactivity, wealth of chemistry and can react with many chemicals that provided multiple bonding sites allowing the load to be transferred onto the nanotubes and better dispersion in the epoxy resin.

The processed amino functionalized MWCNTs had an average diameter of 20 nm and a length of 20-50µm and were mixed with the epoxy resin. The epoxy resin E51 was processed with an aromatic curing agent JX-011 in the ratio of 4:1 and mixed with MWCNTs through sonication process. The three-point bending tests were conducted to determine the flexural strength of the sample prepared. A 2000N load cell and a crosshead speed of 2.0mm/min were used on the samples (60mm x 8 mm x 4 mm). The results from the bending tests indicate that amino functionalized MWCNTs have stronger interfacial bondings that enabled stress to be transferred to the nanotubes resulting in an increase in the flexural strength as compared to the neat resin. The amino (diaminodiphenylmethane) functionalized MWCNT had an improvement of 120% in flexural strength at an addition of 1 wt%. The test results showed that the flexural strength of the composites containing 2 wt% MWCNT is lower than that of composites with 1

wt%, though it is still much higher than that of the neat resin. In addition, SEM analysis was carried out to determine the morphology of fracture surfaces and dispersion of the nanotubes in the matrix. The images illustrated good homogeneity between the epoxy and MWCNTs. It was also observed that a number of bundles were broken rather than pulled out at the fracture surface, suggesting that strong bonding existed between the epoxy matrix and MWCNTs.

Bekyarova *et al.*, (2007a) presented an approach to the development of advanced structural composites based on engineering multiscale carbon nanotube-carbon fibre reinforcement. The carbon nanotube/carbon fibres were successfully infiltrated with epoxy resin using the vacuum assisted resin transfer molding (VARTM) method. During the study, two types of carbon nanotubes MWCNTs and SWCNTs were used for the electrophoretic deposition. The epoxy resin (EPON 862, Hexion Specialty Chemicals, Inc.) was mixed with the curing agent (Epi-Kure W, Hexion Specialty Chemicals, Inc.) at 100/26.4 parts by weight.

The interlaminar shear strength was measured using the short-beam method (ASTM D 2344) by testing small specimens in three point flexure at a span-to-thickness ratio of 4 to promote shear failure between the plies. Therefore, an addition of MWCNTs plays a significant role in the reinforcement of the polymer matrix. The introduction of 0.25% of MWCNTs in the CF/epoxy composites results in an enhancement of the ILSS by 27%. This leads to a multiscale hybrid composite with enhanced out-of-plane mechanical and electrical properties.

Hernandez-Pe' rez *et al.*, (2008) evaluated the mechanical, thermo-mechanical, and electrical properties of MWCNT/brittle epoxy composites using different types of nanotubes. The nanotubes investigated had significantly different aspect ratios and slightly different content of metal impurities. Two types of catalytic MWCNTs produced via CVD with purity >90% were purchased from MER corporation. The first type of nanotubes, hereafter referred to as CSD, have an inner diameter of 3–8 nm, external diameter (d) of 140 ± 30 nm, and 7 ± 2 μ m length (L) and has over 95% nanotube content with amorphous carbon and very small traces of metals (mainly Fe) as impurities. The second type of tubes utilized in this research, hereafter referred to as CMW, has an external diameter of 35 ± 10 nm with approximately 30 μ m length and has over 90% nanotube content with the slightly larger content of metal impurities and amorphous carbon. The epoxy resin used was DGEBA (Epon 828, Shell corporation) and the curing agent was a *m*-phenylenediamine (MPDA, Sigma–Aldrich), an aromatic amine. Nanocomposites consisting of

an epoxy matrix loaded with 1 wt% MWCNTs (either CSD or CMW) were prepared using an ultrasonic bath to disperse the tubes within the matrix. The results indicate that the nanotube morphology and impurity content can significantly affect the effective properties of the resulting composite. It can be concluded from this study that while tensile properties showed very limited improvement, the impact resistance improved by ~84 % (at 1% addition of CMW tubes) and ~63 % (at 1 % addition of CSD tubes) when mixed with resin. Furthermore, fracture toughness improved by a factor of 2.3 for CMW/epoxy composite whereas only ~12.5 % for CSD/epoxy composite.

Kim *et al.*, (2009) presented processing, characterization and modeling of CNT-reinforced multiscale composites. High-energy sonication was used to disperse CNTs in the resin, followed by infiltration of the fibre preform with the resin/CNT mixture. A low CNT loading of 0.3 wt% in resin had little influence on tensile properties, while it improved the flexural modulus, strength, and percent strain to break by 11.6%, 18.0%, and 11.4%, respectively, as compared to the control carbon fibre/epoxy composite.

The CNTs used in this study were XD-grade (i.e. a mixture of single-, double-, and triple-walled nanotubes) characterized by the electrical conductivity suitable for electrostatic discharge application, manufactured by Unidym Inc. The four-harness satin weave IM7 carbon fibre obtained from Hexcel was used as the preform. The matrix material consisted of Epon 862 epoxy resin and EpiCureW curing agent manufactured by Miller-Stephenson Chemical Co. The carbon fibre–epoxy interface was investigated by observing the morphology of the fracture surface using SEM. The SEM images showed weak bonding at the fibre–matrix interface representing fibre–matrix debonding and pullout mechanism. The inter-strand gap also contributed to the reduction in the measured tensile modulus of the composite. Therefore, while sonication is an effective method to disperse CNTs in a resin, duration, intensity, and temperature need to be controlled to prevent damages imposed on CNTs and premature resin curing.

Ye H. *et al.*, (2009) studied the mechanical properties of carbon nanotubes/polymer composite films that were fabricated with different types of CNTs (SWCNT, MWCNT, functionalized few-walled carbon nanotubes (FWCNT)). The reinforcing nano-fillers have been mixed with polyvinyl alcohol (PVA) to form the reinforced composite. The study revealed that the suspension of functionalized CNT and PVA matrix was uniform without any visible

aggregations, while large agglomerates still existed with un-functionalized CNTs. The results also indicate that all of the composite films with as little as 0.2 wt% nanotube showed higher young's modulus and higher tensile strength than those of pure PVA materials. The films with 0.2 wt% FWCNT exhibited the highest young's modulus of 6.33 GPa (1.99 GPa higher than pure PVA film) and 42 MPa increase in tensile strength. It was also concluded that in order to maximize reinforcement, nanotubes with small diameter would be needed to obtain greater surface area and maximized interaction with the matrix. However, the strong intrinsic van der Waals attractions in SWCNT produced large bundles, making them more difficult to be dispersed in any solvent of polymer matrices. In addition, they are extremely difficult to be debundled even after functionalization as compared to FWCNT and MWCNT. The large agglomeration results in the origination of cracks in composites rather than reinforcing the mechanical strength. The research has considered functionalized FWCNT as the optimum candidate for polymer reinforcement as they can be produced easily, uniform structure after functionalization, smaller diameter provides better dispersion, stronger interfacial adhesion and more efficient load transfer between the CNT and the polymer matrix.

Martone *et al.*, (2010) presented reinforcement efficiency of MWCNT/epoxy nanocomposites. Mechanical reinforcement of polymer matrices loaded by CNTs was expected to be benefited both by the high aspect ratio and the very high modulus of such nano-fillers and, consequently, it depends not only on their content within the host system but, also by the state of dispersion. In this paper, they analyzed the effect on the bending modulus of dispersed multi-walled carbon nanotube (MWCNT) into an epoxy system. At the end they concluded that reinforcement efficiency is characterized by two limiting behaviors whose transition region coincides with the development of a percolative network of nanotubes.

Ramana *et al.*, (2010) has illustrated the effect by varying the proportion of CNT on the flexural properties of the composite. The nanocomposites were developed by mixing CNTs (0.2 – 1 wt%) of the epoxy and homogeneously dispersed in ultrasonication bath for 1 hour. Pristine CNTs and Epoxy AW-106 were mixed together and Epicure Curing Agent HV 953 was later on added using a mechanical stirrer for 10 minutes. The mix ratio of epoxy to curing agent was 4:1. After the mixing was performed the SEM images revealed the numerous entangled carbon nanotubes. In order to carefully observe the nature of the functional groups and defects on the surface of the

nanotubes, X-ray photoelectron spectroscopy (XPS) techniques were used. The results suggest that the dispersion of CNTs in epoxy is limited to 1 wt%, whereas, higher amount of filler materials causes more agglomerates of CNTs which leads to inhomogeneous dispersion. The viscosity of the acid treated CNTs reinforced composites were increased as compared to pristine CNTs for the same amount of filler material. In addition, the three point bending test was also performed on the specimens and the results indicate that by increasing the weight percentage of CNTs there is an increase in the flexural strength of the composites. Addition of 1 wt% of pristine CNTs had a flexural strength of 77 MPa and the addition of 1 wt% functionalized/chemically treated CNTs had a significant improvement in flexural strength i.e. 104 MPa. Therefore, functionalized CNTs are more effective as reinforcing agents. The SEM images revealed that EP GFRP composite failed in a catastrophic mode, whereas, the composite made with pristine CNTs had macroscopic cracks that continued to propagate ultimately leading to the failure of the whole composite sample. Whereas, in the case of functionalized CNTs these cracks occurred on the interface between CNTs and fibre pullout and composites failed at a very high load.

Sanchez *et al.*, (2013) prepared carbon fibre composites with epoxy matrices modified with different CNT contents (0.1, 0.2 and 0.3 wt%) along with different surface conditions (i.e. non-functionalized and amino functionalized) in VARIM mold. The incorporation of nano-fillers into the resin increased the viscosity values, this effect was more severe for non-functionalized CNT/epoxy composite. It was stated that the viscosity of resin should not be higher than 1000 mPa-s for suitable infiltration by VARIM. Also an increase in temperature during the processing causes an increase in temperature of the resin and results in a decrease in viscosity. The tensile and flexural tests were carried out to study the mechanical behavior. Elastic modulus was found to be unaffected by the addition of CNT and it was independent of the surface condition of the CNT. Tensile strength increased for non-functionalized CNT composites and decreased for AMWCNT composites. It was seen that amino groups on CNT led to the formation of agglomerates and behaved as stress-concentration points resulting in lowering the tensile properties. However, stress-strain curves showed an increase in fracture elongation for all tested multiscale composites, which was higher in the case of those reinforced with amino functionalized CNTs. Stress-strain curves were also plotted for flexural tests and they showed a large linear deformation zone (up to 2% approximately of deflection) followed by a second zone

with irregularities that can be attributed to out-plane fibre breakage during loading. It was seen that 3-point bending test was more sensitive to the behavior of the matrix. Flexural modulus is dependent on the fibre content. CNT-NH₂ composites showed an increase in flexural modulus. Functionalized CNT have increased shear strength that caused an enhancement in flexural modulus as a better interface was available to transfer the load from matrix to CNT. For functionalized CNT composites increase in flexural strength was also observed, but stepped up shape was less evident probably due to inhibited matrix cracking and local delamination. Whereas, non-functionalized showed an all time increase in flexural strength as compared to functionalized CNT, which showed an increase only at higher concentrations.

Nanoreinforcements provided a mechanism of matrix strengthening, such as crack bridging which was more effective for functionalized nanotubes. Interlaminar-shear-strength (ILSS) values increased up to 0.1 wt% for non functionalized CNT and decreased on further addition of CNT possibly due to the presence of void contents and higher viscosity of the mixture. Whereas, amino functionalized CNT showed an increase of 10% in ILSS at 0.3 wt%. FEG-SEM images for non functionalized CNT composites illustrated shear fracture of epoxy matrix and fibre matrix debonding as the main failure mechanism. The presence of CNT is detected in matrix transverse cracks and pullout phenomenon. However, for functionalized nanotubes delaminated surfaces showed a higher interaction between the matrix and fibres. Cohesive failure modes were detected through the matrix. Also, less developed 'shear hackles' were observed that were a signal of low deformation by shearing. The nanotubes broke with low extraction lengths and were coated by a matrix layer due to the stronger bond formed between the CNT and the epoxy by amino groups.

Dalina *et al.*, (2014) prepared E-glass fibre (GF) and Carbon fibre (CF)/Epoxy/MWCNT composites and compared the properties between 5 and 4 ply laminate composites. The CNT was added to epoxy resin via ultrasonicator at 24kHz, 50% amplitude for 30 minutes. Hardener amount was calculated and added to the mixture again using ultrasonicator for 10 minutes. CNT concentration was chosen to be 0.5, 1.0 and 1.5 wt%. The results found that the density decreased with the addition of MWCNT as compared to 5-ply specimen (14% and 8% for GF, CF respectively). Use of 4 plies in sample preparation also results in weight reduction while

providing adequate strength and stiffness. It was also found that composites prepared with GF have higher density than CF due to nature of GF itself.

On the other hand, flexural strength reduced by 25% for GF/epoxy and CF/epoxy laminates when plies were reduced from 5 to 4. Addition of 0.5 vol% of MWCNT in epoxy, 4ply GF improved flexural strength by 54.4% as compared to 5-ply GF. Whereas, the addition of 1.5 vol% MWCNT results in reduction of flexural strength due to agglomeration of MWCNT. It also caused the void formation and increased the viscosity of the mixture. Moreover, the addition of 0.5 vol% MWCNT in GF composite increased flexural modulus by 0.2% and 16% as compared to 5-ply GF and 4-ply GF composite respectively. Lastly, it was also found that the incorporation of MWCNT in epoxy resin reduces the burning rate, as CNT serves as a heat shield for virgin polymer below the layer. It limits the transfer of volatile gas. Hence, CNT can also be used in future as a heat-shield in various industrial applications.

Hossain *et al.*, (2014) prepared composites with Carbon fibre/Epoxy/CNT. The CNT was XD grade, which consists of SWNT and DWNT amino functionalized along with carbon black and metallic impurities. The concentration of amino functional groups was <4%. The CNT concentration was chosen to be 0.5, 0.4 and 0.3 wt%. Mixing of epoxy and AMWCNT resulted in interfacial reaction creating a cross-linking between amine and epoxide groups. The cracks were not able to propagate in nanocomposites due to the presence of CNT. Large volume of pull-out nanotubes were observed, which slowed down crack propagation and changed its path. In ILSS test, failure occurred due to a combination of interlaminar shear cracking, microbuckling, indentation and fibre rupture. The silane treatment of CF was done to make a durable bond between the fibre and matrix. Once a silane was covalently bonded to the surface of the fibre it allowed wide range of chemical reactions with epoxy and amine groups on CNT. The covalent bonding, increased the interfacial bonding and thus improved ILSS of the composites. Moreover, the storage modulus increased by 17.22% at 0.3 wt% XDCNT and loss modulus also increased for the same concentration. However, storage modulus decreased above 120°C due to the easier movement of polymer chain. T_g also increased for 0.3 wt% XDCNT in the composite. Whereas with CNT concentration at 0.4 wt% agglomerates were present that resulted in degradation of the properties, interfacial adhesion between the nano-fillers and matrix was lowered and molecular mobility was higher. It was also found that functionalized CNTs provide better dimensional

stability than pristine ones. From the SEM results it was analyzed that at 0.3 wt% it showed only matrix cracking (resulting in an increase in ILSS). However, at 0.15 and 0.4 wt% combination of delamination and cracking at matrix interface were observed. Lastly, high concentration of CNT resulted in high viscosity of resin and caused poor wetting during laminate fabrication and poor adhesion between the carbon fibre and matrix. However, the presence of amino groups on XDCNTs surface promoted good adhesion between CF and epoxy matrix.

Tzounis *et al.*, (2014) prepared nanocomposites by two different methods i.e. grafting of MWCNT on the glass fibre surface and incorporation of MWCNT in the matrix. GFs were chemically treated with a basic piranha solution to purify fibres and increase the number of silanol groups on the surface by hydrolysis of siloxane network. GFs were treated with aminopropyltriethoxysilane (APS) 1% in extra dry toluene. MWCNT were functionalized with –COOH group and grafted onto GF surface. TEM images showed that MWCNT-COOH acid treatment generated surface defects and no smooth surface of the outer wall was observed. XPS results showed an increase in the amount of nitrogen on sample surface due to silane treatment of GF. SEM images showed neat and smooth surface after basic piranha treatment due to the possible hydrolysis of siloxane bonds. APS treated GF showed mountain-like topography due to the condensation of silanes on the surface of GF.

Grafted MWCNT on GF showed highest interfacial adhesion strength, i.e. 65.4 MPa with an increase of 48% as compared to GF-APS. A plausible explanation is that epoxy monomer interdiffused through CNT grafted network and chemically interacted with both amine groups of GF via nucleophilic ring opening reaction, as well as with carboxyl groups of MWCNT via esterification. This results in an improved load transfer from the matrix to nanotubes and caused an overall improvement in Interfacial-shear-strength (IFSS). Furthermore, SEM images showed cohesive failure since the matrix material was observed on the fibres after pull-out process. Lastly, the nanoscale roughness on the glass fibre surface can further introduce a mechanical interlocking mechanism which was seen in the case of grafted MWCNT as compared to as-received glass fibres.

The literature review on CNT polymer nanocomposites has been summarized in Table 2.1 in a chronological manner.

Table 2.1: Summary of literature review related to CNT modified FRP

S.No.	Material	Processing	Key results	Reference
1.	CNT: DWCNT, DWCNT-NH₂ (Belgium), Diam: 2.8nm Epoxy: DGEBA, L135i Hardener: Amine, H137i Low viscosity = 250 mPa-s Glass fibre	Manual mixing of nanoparticles in the epoxy matrix and transferred to mini calander for final high shear mixing. Degassing for 20 mins was done before infusion and after the addition of amine hardener Curing as per epoxy resin. Post Curing was modified to 80⁰C. Tensile test – DIN EN 527.1/2 in 0 and 90 degrees.	TEM images showed well separated and impregnated DWNT-NH₂ with epoxy resin. On increasing CNT concentration it led to increased viscosity and processing problems. GF shows fibre dominated behavior of tensile prop after addition of amino functionalized CNT. Degassing caused re-agglomeration of nanotubes (because SA increases) Tensile prop least affected by addition of amino functionalized CNT. ILSS properties increased significantly, i.e. 20% at 0.2 wt% DWCNT-NH₂ (due to nano reinforcement, amino groups caused cross linking with an interface which increased interfacial strength).	Gojny <i>et al.</i> , 2005b

			ILSS for neat epoxy (EP) = 31.8 MPa, for 0.1 wt% CNT = 36.8 MPa and for 0.3 wt% CNT = 38.1 MPa SEM images showed DWCNT-NH₂ located in matrix rich areas. Orientation of nanotubes indicates that final failure occurred under pullout or rupture of the CNT.	
2.	CNT: MWCNT (diameter – 15 nm), DWCNT, DWCNT-NH₂ (diameter – 3 nm and length – 10 μ meter), Nanocyl Belgium Epoxy: L135i and hardener H137i (DGEBA) Carbon black (XE2, Germany), Fumed silica nanoparticles (Aerosil A380, Germany) with diameter – 7 nm Glass fibre: non-crimp fabrics 37% and 50 vol% were	Fumed silica nanoparticles were treated with GPS. Nanoparticles dispersed in epoxy matrix using high shear mixing process (mini-calander) GFRP were prepared via RTM process. The resin/particle suspension was degassed before injection. Curing for 24 h at room temperature and	All nanoparticles significantly increase ILSS, DWCNT showed a maximum increase (38.7 MPa). Application of electric field further increased ILSS. ILSS decreases with increase in higher GF volume content. In 37 vol% GF, crack propagates through fibre-free matrix areas and crack are mostly interlaminar. In 50 vol% GF, it shows tendency for translaminar crack propagation due to weak fibre-matrix interface. Dominating failure mechanism in mode I test was	Wichmann <i>et al.</i> , 2006

	chosen Silane: 3-glycidyloxypropyltrimethoxysilane (GPS), Germany and provides epoxy group on surface of the particle	post-curing at 80°C for 15 h. Electric field applied during curing process for the orientation of nanotubes to fibre-plane direction at 330 V/cm.	GF-matrix interface failure.	
3.	MWCNT: diameter 10-20 nm, length 10-50 μ meter (0.05, 0.1, 0.25, 0.5 wt%) Epoxy: Epon 828 (DGEBA) Hardener: m-PDA Ratio: 14.5:100 Silane: GPS	f-CNT were added in ethanol for 1 h and sonicated for 1 h at 60°C before adding to epoxy. Epoxy was added to mix and ultrasonicated for 1 h at 80°C. Degassed the mix at 80°C for 5 h. Hardener was added. Cured on a flat plate at 80°C for 2 h and post curing at 150°C	SEM results: Silane CNT showed uniform dispersion in epoxy matrix. Converts CNT surface from hydrophobic to hydrophilic. Thermal decomposition of silane CNT/epoxy composite was retarded due to silane CNT. Thermal stability increased for 0.25 wt% silane CNT at elevated temperature. Stronger effect on storage modulus and tan delta in rubbery region at elevated temperature. Maximum Tan delta was observed for neat epoxy sample. Increase in loss modulus for silane CNT. T_g increases with addition of	Ma <i>et al.</i> , 2007

		for 2 h. Silane f-CNT was also prepared.	CNT and further with silane CNT. Elastic modulus increased up to 0.25 wt% in epoxy matrix and silane CNT showed even further increase in flexural strength. An increase was up to 0.25 wt% CNT and decreased on further increase in concentration Fracture resistance decreased for untreated CNT in epoxy and increased for silane treated CNT. Silane treated CNT revealed a systematic increase in number of river markings and corresponding surface roughness with increase in CNT content. At low concentration (0.05 – 0.1 wt %) it showed straight and long river markings running parallel to crack propagation. Whereas, at high concentration (0.25 – 0.5 wt%) shorter and round-ended were visible. Fracture toughness showed	

			maximum up to 0.5 wt% CNT	
4.	Hybrid MWCNT/ GFRP composites.	Mechanical stirring, ultrasonic agitation and acid oxidation to create a well dispersed MWCNT suspension VARTM, Injection and Double Vacuum Assisted Resin Transfer Molding (IDVARTM).	Uniform distribution of Oxidized MWCNT (OWMCNT) between fibre layers, using suspensions of up to 2 wt% OMWCNT epoxy with IDVARTM. Improved Interlaminar shear strength in composites.	Fan <i>et al.</i> , 2008
5.	Woven Roving Glass fibre (0.28 mm thickness) /MWCNT/epoxy nanocomposite.	Epoxy resin blended with 1 wt% CNT, Wet layup method for manufacturing laminated [0/90] composite. 8 plies of glass fibre were wetted in a heated platen press at 580 kPa	Addition of 1 wt% MWCNT significantly improved high-cycle fatigue strength by 60 – 250%. No effect on the elastic modulus, but a slight increase in strain to failure was observed. Addition of CNT into the matrix inhibits the formation of large cracks since a large density of nucleation sites are	Grimmer <i>et al.</i> , 2008

		for 1 h.	provided by CNT. SEM images suggested CNT pull-out and fracture mechanism.	
6.	Amino functionalized MWCNT, Epoxy and T-31 hardener	Pristine MWCNT functionalized with amino group (a-MWCNT) a-MWCNT (0, 0.1, 0.5, 1.0, 1.5, 2.0 wt%) mixed with acetone and sonicated for 1 hr epoxy added using sonication for 5 hr acetone evaporated in vacuum oven at 80C for 1 hr T-31 add using stirring at 2000 rpm for 15 min Degassing at 80C for 2 hr	FTIR peaks confirmed the presence of carboxyl and amino groups onto the surface of MWCNT. Tensile strength of EP was 39.12 MPa but it increased to 59.2 MPa for a-MWCNT. Whereas, the impact strength was 5.5 kJ/m² for EP and 10.6 kJ/m² for a-MWCNT samples. Tensile and impact strength started decreasing after 2 wt% concentration. SEM images of tensile strength specimens showed broken CNT instead of pull-out. Thermal decomposition and glass transition temperature increased with addition of a-MWCNT (due to low mobility of epoxy moiety when it reacts with amino	Chen <i>et al.</i> , 2008

			groups).	
7.	MWCNT, Length: 10 – 20 μ meter (0.02, 0.05, 0.2, 0.5, 1.0, 2.0 wt%) Epoxy: DGEBF, D.E.R. 354, Dow Chemicals Hardener: DETD, ETHACURE 100, low viscosity of 2-3 mPa s. (31.14:100) Solvent: Ethanol	Pristine CNTs were acid treated to produce carboxylic groups on the defect sites MWCNT-COOH was dispersed in ethanol and epoxy was added using probe for 15 min (600W m/c). Degassed mix at 60⁰C for 5 h. Hardener was added. Curing at 80⁰C for 8 h then 130⁰C for 10 h. For cryogenic temperature →dispersed in liquid nitrogen cryostat i.e. 77K	CNT are good reinforcement for polymers at cryogenic temperature than at room temperature (RT). MWCNT/epoxy composite was ductile at room temperature as compared to 77K. Epoxy resin showed brittle behavior at 77K for all composites. MWNT/epoxy composite tensile strength decreased for 2 wt% at RT (due to poor bonding between matrix and CNT). Maximum tensile strength obtained at 0.5 wt% at 77K – even higher as compared to RT sample (119.35 MPa/ 74.4 MPa). Possibly due to stronger interfacial bonding, chemical bond between epoxy and CNT shrink thus, more energy is required to break the bond. Impact strength also increases	Chen <i>et al.</i> , 2009

			up to 0.5 wt%. Young's modulus increases at 77K due to lower mobility of molecules, also CNT/matrix becomes stiffer. High CNT concentration also results in reduction of failure strain. Fracture surfaces become rougher after CNT addition.	
8.	MWCNT (CVD produced) Carbon fibre – Thornel T650 EPIKOTE 862 Resin and EPIKURE Curing Agent W	Resin mixed with curing agent in 100:26.4 by weight. Single fibres were placed with notches in molds and epoxy was poured into the mold. Specimen were placed in an oven and cured for 2 h at 121⁰C and then more for 2 h at 177⁰C. Surface was polished with 0.5 µm alumina.	Tensile strength decreased by 37% for radially aligned MWCNT and 30% in randomly aligned MWCNT. The reduction occurred due to the addition of surface flaws to fibre through thermal degradation and surface oxidation. Randomly oriented and aligned MWCNT demonstrated a 71% and 11% increase in interfacial shear strength over untreated, un-sized fibres.	Sager <i>et al.</i> , 2009

9.	MWCNT, thin-MWCNT (TMWCNT) and DWCNT amine group functionalized. DGEBA Epoxy Resin and DICY – Aradur 5021 hardener Carbon fibre with 800 Tex	0.5 wt% CNT was dispersed using high-shear calendaring technique. 8 peel plies were laid in unidirectional fibre orientation. Laminates were produced in an autoclave at 0.65 to 0.70 bars. Curing for 60 min at 120⁰C and post curing at 140⁰C for 120 min. High-shear mixing Prepreg technique.	The coefficient of thermal expansion decreased by 32% with addition of DWCNT in matrix. Mode-1 fracture toughness improved by 80% for pristine MWCNT in combination with epoxy resin modified using a compatibilizer. Longitudinal tensile strength decreased by 20 % with addition of CNTs – due to stress build up around the broken fibres. Decrease of ILSS for MWCNT, TWCNT and DWCNT was reported due to poor interfacial interaction with the matrix. ILSS increased for modified-MWCNT composite up to 65 MPa. Increase in fracture toughness values with addition of CNTs and crack initiation energy by 75%.	Godara <i>et al.</i> , 2009
10.	Matrix: DGEBA Curing agent: DDM CNTs: MWCNT-	CNT first dispersed in chloroform	Presence of CNTs has a retardation effect on the epoxy curing reaction.	Prolongo <i>et al.</i> , 2010

	NH₂, from Nanocyl, Belgium Functionalized with amino groups (0.5 wt% amino)	Epoxy resin was added to the solution mixed by high-shear mixing at 150 rpm for 30 min at 45°C. Resulting solution was sonicated for 45 min using 50-60 Hz sonicator. Solvent was evaporated by using stirring in vacuum at 90°C during 24 h. DDM was added into mixture by stirring at 85°C for 3-5 min. CNT in 0.1 and 0.25 wt% was added Procuring treatment of epoxy/CNT was carried out at 130°C for 1 h to favour chemical	The adsorption of curing agent molecules inside the nanotubes causes a decrease of reaction heat for the epoxy nanocomposites. The retardation effect of CNTs is mainly associated to the decrease of autocatalytic constant due to the higher difficulty to form ternary complexes. The glass transition temperature of epoxy matrix increases by the addition of CNTs due to the restriction of its mobility. T_g is higher for amine excess composition	

		reaction between amino groups of CNTs and oxirane groups of epoxy. Stoichiometric ratio was also varied		
11.	MWCNT-COOH: diameter 5-15 nm, >95% purity Epoxy: Epon 828 (DGEBA) Hardener: EMI-2,4 (6% by weight of DGEBA) Silane: amino silane A1100	Silane treatment of MWCNT-COOH and 7.3 wt% was added (show better dispersion and are homogeneous). Stir DGEBA-absolute ethanol solution at 80°C with magnetic stirrer for 20 min. MWCNT was added to solution and continuously stirred for 30 min and sonicated for 1 h. Solution was cooled to 60°C. Hardener was added and stirred	FTIR confirmed 56% modification by silane treatment. As-received MWCNT-COOH agglomerated severely whereas, silane treated MWCNT were well dispersed and depicted homogenous distribution. Weak interfacial bonding between MWCNT-COOH and epoxy resulted in nanotubes being pulled-out of the surface. Addition of MWCNT-COOH delayed the thermal degradation of epoxy hardener mixture system. On the other hand, silane MWCNT-COOH nanotubes	Zhou T <i>et al.</i> , 2010

		for 10 min. Mix was degassed in vacuum oven at 60⁰C. Curing at 65⁰C for 1 h, 120⁰C for 1.5 h and 160⁰C for 1.5 h. Solution was finally cooled down to room temperature and then demoulded. Thermal degradation using TGA at 10⁰C/min to 750⁰C in N₂ atmosphere.	decreased the thermal stability of MWCNT-COOH/Epoxy hardener composite.	
12.	MWCNT, thin MWCNT and DWCNT (amine functionalized) Amino MWCNT Epoxy -DGEBA and Aradur 5021 hardener Carbon fibre with 800 Tex	0.5 wt% MWCNT was dispersed in epoxy matrix. Unidirectional laminates were prepared in autoclave at 0.65 – 0.70 bar vacuum and cured at 120⁰C	Combination of compatibilizer with un-functionalized MWCNT increased toughness by 75% and suggests optimal dispersion and interfacial interaction. Improved Interfacial shear strength of MWCNT- glass fibre epoxy composite. Increase in the damage	Gorbatikh <i>et al.</i> , 2011

	E-glass fibre	for 60 min and post curing at 140 ⁰ C for 120 min. RTM	threshold in MWCNT- carbon fibre epoxy composite was also reported	
13.	SWCNT produced using in-house double laser method Epoxy Resin: Bisphenol A	0.1 and 0.2 wt% SWCNT was integrated into epoxy resin and manufactured using an autoclave after hand lay-up and vacuum bagging of prepreg plies.	Incorporation of 0.1 wt% of SWCNT resulted in a 5% reduction in impact damage area, 3.5% increase in compression after-impact strength. 13% increase in mode-I fracture toughness (due to crack bridging), and 28% increase in mode-II Interlaminar fracture toughness (due to formation of larger hackles). The fracture toughness increased in mode-II because CNT act as rigid fillers that prevent the crack, delaying the expansion of micro-crackling within matrix interface area. SWCNT are more effective in enhancing the mechanical performance.	Ashrafi <i>et al.</i> , 2011
14.	SWCNT and	Amine groups	Binding energy of	Milowska

	Graphene layers (GL) functionalized with – NH and – NH ₂	have been added uniformly on the surface of SWCNT	functionalized CNT and GL increases with the increasing density of the functionalizing molecules i.e. binding of –NH is more stronger than –NH ₂ Young's Modulus diminishes more for the functionalized SWCNT as compared to functionalized GL. Amines exhibit strong cohesion to CNTs and graphene monolayer.	<i>et al.</i> , 2012
15.	Matrix: poly (methyl methacrylate) PMMA CNT: MWCNT	Molecular study to evaluate the elastic properties of the interfacial region between CNT reinforcements and polymer composites when subjected to tension. Effect of aspect ratio of CNT fibres on the elastic properties and interfacial bonding is also	Simulation results demonstrated that the Young's modulus of a PMMA composite when reinforced by infinite long (5, 5) CNT increases to 46.73 GPa, which is 16 times stiffer than a pure PMMA material. Strength of CNT/PMMA composite also increases with an increase in the aspect ratio of CNT fibres	Arash <i>et al.</i> , 2014

		studied		
16.	Matrix: DGEBA Curing agent: polyamine hardener with mixing ratio of 100:15 MWNCTs: vapor grown, D: 10-20nm, L: 5-15µm Fibre: glass fibre chopped strand mat	Hand mixing of 0.5 wt% MWCNT in epoxy Followed by sonication at different powers and durations Hardener was added to the mixture and poured into the steel molds. Hand lay-up method employed to fabricate sheets of MWCNT/CSM/Epoxy nanocomposites	With an increase in sonication time there was an increase in Young's modulus but, dropped for longer sonication times Highest Young's modulus was attained for sonication power of 50W and time of 45 min. Highest tensile strength was obtained for power of 25W and time of 45 min. Sonication at 50W for 15 min resulted in highest value of T_g. Well dispersion was observed as power and duration of sonication was increased.	Montazeri and Chitsazzadeh, 2014
17.	Matrix: polyester MWCNT: CVD grown, D: 10 to 20 nm, L: 5-15µm Fibre: glass fibre with chopped strand	Curing process was performed by addition of cobalt ethyl ketone peroxide Mechanical	Low sonication time did not have the ability to disperse MWNTs fully in polyester resin Flexural strength of MWNT/CSM/polyester composite enhanced by 45%	Shokrieh <i>et al.</i> , 2014

	mat	stirring (20 min at 2000 rpm) was used for breaking agglomerates of MWCNT in polyester. It was followed by sonication to disperse them in the matrix. After obtaining optimum sonication time, hardener was added to the mixture and immediately the nanocomposites were fabricated by hand lay-up technique.	at only 0.05 wt%. Tensile, flexural and compressive moduli of composites improved at 0.3 wt% MWNT content. At higher concentrations it resulted in poor dispersion, increase in mixture viscosity, and degradation of mechanical properties.	
18.	Polyaniline/ZnO	Composites were synthesized by in-situ polymerization of aniline using various compositions (10, 20, 30, 40, 50	XRD analysis shows the amorphous nature of the composite SEM images revealed better dispersion of ZnO in PANI matrix. Thermal analysis shows higher thermal stability of	Goyal <i>et al.</i> , 2015

		wt%) of ZnO in PANI matrix.	PANI/ZnO composites than pure PANI. dc electrical conductivity of PANI/ZnO composites decreased as ZnO content increased in PANI but, increased with the increase in temperature.	
19.	Matrix: DGEBA Curing agent: Aradur 5021 CNT: MWCNTs (Nanocyl – 7000 series), D: 9.5nm, L: 1.5 μm purchased from Belgium Fibres: carbon	0.5 wt% MWCNT was added into epoxy resin using 3-roll calendaring equipment 6 different composites were prepared: carbon fibre/epoxy composites with and without CNTs in matrix, with and without CNTs in fibre sizing, with varied content of CNTs in the fibre sizing	Adding CNTs into fibre sizing improved the fibre-matrix interface. If CNTs are added only in fibre sizing and not in matrix, the delamination damage begins in the interface CNTs if added in matrix, improves the bonding capacity of fibre sizing and the matrix, toughness and resistance to delaminating crack propagation. Adding CNTs into the matrix also ensures high strength of the material. ILSS increased by 77% for virgin sizing of fibres Addition of CNTs in both matrix and fibre sizing results in 36%-53% increase in	Zhou HW <i>et al.</i> , 2016

			toughness of the composite and in ILSS by 42% - 88%. High volume content of CNTs is better for sizing. And its effect is strongest for small loading in matrix along with high content in fibre sizing.	

2.2 Silane treatment of glass fibres

The aim of the silane treatment is that the silane coupling agent should establish a strong interfacial bond between epoxy resin and glass fibre mat. The literature for silane treatment of glass fibres with either 3-glycidylpropyltrimethoxysilane (GPS) or 3-aminopropyltriethoxysilane (APS) has been summarized in Table 2.2.

Table 2.2: Selected studies on reinforcement of silane treatment of glass fibres in either neat epoxy or CNT-modified epoxy matrix system

S.No	Material	Processing	Key results	Reference
1.	GF, aminopropyltriethoxysilane Epoxy resin	An aqueous solution of diethyl phosphite was applied on GF surface to improve bonding strength. This improves the dry strength of the laminates. To improve the wet strength glass laminates should be treated with gamma – aminopropyltriethoxysilane solution. Laminates have been	Method for improving wet strength of GF to resin: GF is made to contact with 1% aqueous solution of gamma aminopropyltriethoxysilane for 2 min and allowing solution to dry on GF plies are immersed in aqueous solution of diethyl phosphite for 2 min and allowing plies to dry on	US 3404023 (1968)

		prepared by immersing GF in 1% aqueous solution of diethyl phosphite for 2 min and removed from solution and allowed to dry overnight. After drying plies are heated in an oven between 110⁰C and 150⁰C for 5-10 min to set the solution on the surface of GF. Laminates are preliminarily treated by immersing them in a 1% APS for short time period and allowed to dry and oven heated all under same conditions as described earlier. Strength can be further increased by rinsing the preliminarily treated plies in distilled water for 4 h.	Plies are subjected to heat treatment between 100 – 150⁰C for 5 – 10 min to set residues of solution on the surface of glass.	
2.	E-Glass (WE18W) – plain woven fabric Vinyl ester resin – Ripoxy R806 γ-glycidoxypro	Silane coupling agents were acidified with acetic acid at pH 4.0. GF were dipped into aqueous solutions of silane agents and squeezed between rollers and dried for 10 min at 110⁰C. 20 ply laminates prepared using hand lay-up technique.	Concentration of silane agent determines mechanical performance and damage behaviour of the composite. Application of silane agent makes the composite more durable in hygrothermal environment. 0.4 wt% GPS showed stable	Hirai <i>et al.</i> , 1998

	pyltrimethoxysilane (GPS) – 0.4 wt%	Laminates cured for 48 h at room temperature, post curing for 3 h at 80 ⁰ C and 2 h at 150 ⁰ C in an oven.	crack growth with plateau fracture toughness. Impact energy = 19 – 47 J At maximum load, major fibre breakage occurred through laminate thickness starting from back face towards the front face On increasing impact energy damage became more extensive in form of matrix cracking, transverse fibre fracture and delamination Laminates with 0.4 wt% GPS had much larger damage area than other laminates.	
3.	Epoxy: DER 331, Bisphenol A Hardener: DEH 26, amine (DOW Chemical's) Fibre: E-Glass, diameter 12 µmeter Silane:	Fibres were heat-cleaned by heating as-received fibres at 500 ⁰ C for 5 h. APS treated fibres were prepared by treating heat-cleaned GF. 2 wt% solution was prepared by dissolving liquid APS in acidified water (pH = 3.5) for 2 h. GF were immersed in APS solution for 10 min and dried at room temperature for 24 h.	Composite samples uptake water about 40 – 60% in first wet step. It absorbs 5-20% more in second wet step and up to 20% more in third step. Epoxy-GF interface is most vulnerable part of composite to moisture attack. Water intake is slow in APS treated GF because of microvoids at interphase are reduced by formation of	Noobut and Koeing, 1999

	Aminopropyl triethoxysilane (APS)	Micro-composite was prepared by dropping 4-5 drops of 1% solution of Epoxy and hardener (weight ratio = 189:27) in acetone on a single GF aligned on a ZnSe disc. Composite sample was stored in vacuum oven for 7 days and post-cured at 70⁰C for 90 min. Hygrothermal conditions: wet exposure by keeping samples in a closed chamber for 40 days at 90±5%RH. Next they were put in vacuum oven at room temperature for 2 weeks. Wet-dry cycle with 30 day wet step and 2 week dry step was repeated for 2 cycles.	chemical bonds between GF and epoxy due to the silane coupling agent. Amino group of APS forms a chemical bond to an epoxide group of epoxy by a ring-opening reaction. Siloxane bonds act as water repellent. Epoxy resin interacts via hydrogen bonding with untreated GF and with treated GF via both hydrogen and chemical bonding. Epoxy/GF interaction is more uniform along GF that in turn makes the degree of the curing in the interphase region more uniform. GF surface degrades when exposed to liquid water or humidity because of leaching out of metal ions from GF. These metal ions may enhance addition of ring-opening polymerisation.	
4.	E-Glass (WE18W) – plain woven fabric	Indentations were made on the specimen at 400 mm apart and 60 nm depth Scratch test was carried out	Silane agents on GF surface help protect the GF surface and act as coupling agent to promote adhesion with	Kim <i>et al.</i> , 2001

	Vinyl ester resin γ-glycidoxypyrtrimethoxysilane (GPS) – 0.4 wt%	by moving the sample while in contact with indenter tip, $W = 2.5 \text{ mN}$ (normal force) applied continuously and frictional force was recorded	polymer matrix. Decrease in T_g as silane content increases due to the cross-linking density of the mixtures. Ability of silane agent to inter-diffuse into and to chemically react with bulk matrix also affects the thickness of the composite which further affects the mechanical performance and behaviour of the composite. Increase in modulus was observed with increased silane concentration as it modified the resin surrounding the fibres. GPS silane treated GF showed smallest interphase thickness (as this silane agent migrates to fibre surface during curing)	
5.	E-Glass fibre from VERTROTE X Epoxy:	E-GF was heat cleaned at 450°C for 1 h to remove any organic substances such as sizing or impurities from the surface.	For epoxy based composite, amino silanes are beneficial as it provides an addition of amine hydrogen to the epoxy ring.	Iglesias <i>et al.</i>, 2002

	TRIEPOX (DGEBA) Hardener: ethylendiamine Silane agents: 3-aminopropyl dimethylethoxysilane (APMES) 3-aminopropyl methyldiethoxy silane (APDES) 3-aminopropyltriethoxysilane (APTES) Fluorescence meas: GF were labelled with dansyl moiety that reacts easily with amines to yield	Fibres were then chemically coated with amino silane coupling agent. 1g of GF was immersed in 50 ml of silane 1% (v/v) aqueous solution for 10 mins at room temperature. After squeezing, fibres adsorbed silane when cured at 110⁰C for 1 h in order to accelerate condensation reaction and to remove water. Remaining silane monomers were removed by subjecting them to a Soxhlet extraction with dry toluene for at least 4 h and vacuumed for at least 8 h. Specimens were immersed in double distilled water at 50⁰C controlled by means of a thermostatic bath. Effect of moisture was done by submerging the samples for 15 and 46 h.	Fluorescence molecules can be used as a method to analyze the interface on a molecular level. APDES and APMES have Young modulus 5 or 6 times higher than EP and APTES sample. The rigidity of materials is reflected by the rigidity at the interface. Therefore, if the amine groups are more accessible, there will be higher cross-linking and will result in greater rigidity. When GF are silanized surface free energy decreased by 30%. Neat resin and APMES showed adhesive failure while APDES and APTES showed cohesive failure. All samples followed Fick's law of diffusion. Silane treated GF show similar amount of water absorption while neat resin shows higher water intake (because non silanized GF have	

	DNA. Hygrothermal in distilled water		greater hydrophilic surface). After 15 h of immersion sufficient water diffuses at interface to completely change sample properties Hydrolysis rate of glass-silane siloxane linkages, Si-O-Si is greater than that of Si-Si linkages. After 46 h of exp to water fibres have smooth and clean surface without presence of any polymers and undergo adhesive failure. Fluorescence band undergoes a blue shift when rigidity increases. Rigidity increases in following order: APTES<APDES<APMES.	
6.	MWCNT: diameter 10-20 nm, length 10-50 μ m (0.05, 0.1, 0.25, 05 wt %) Epoxy: Epon	F-CNT were added in ethanol for 1 h and sonicated for 1 h at 60⁰C before adding to epoxy. Epoxy was added to mix and ultrasonicated for 1 h at 80⁰C. Degassed the mix at 80⁰C for 5 h.	SEM results: Silane CNT showed uniform dispersion in epoxy matrix. Converts CNT surface from hydrophobic to hydrophilic. Thermal decomposition of silane CNT/epoxy composite was retarded due to silane CNT. Thermal stability	Ma <i>et al.</i>, 2007

828 (DGEBA) Hardener: m-PDA Ratio: 14.5:100 Silane: GPS	Hardener was added. Cured on a flat plate at 80⁰C for 2 h and post curing at 150⁰C for 2 h. Silane f-CNT was also prepared.	increased for 0.25 wt% silane CNT at elevated temperature. Stronger effect on storage modulus and tan delta in rubbery region at elevated temperature. Maximum tan delta was observed for EP sample. Increase in loss modulus for silane CNT. T_g increased with addition of CNT and further with silane CNT. Elastic modulus increased up to 0.25 wt% in epoxy matrix and silane CNT showed even further increase. Flexural strength increased up to 0.25 wt% CNT and decreased on further increase in concentration. Fracture resistance decreased for untreated CNT in epoxy and increased for silane CNT. Silane CNT revealed a systematic increase in number of river markings

			and corresponding surface roughness with increased CNT content. Low concentration (0.05 – 0.1 wt %) showed straight and long river markings running parallel to crack propagation. High concentration (0.25 – 0.5 wt%) shorter and round-ended. Fracture toughness showed max up to 0.5 wt% CNT.	
7.	MWCNT – CVD grown, Diam: 10-20 nm, Length: 10 – 15 μ m (0.025, 0.05, 0.06, 0.08, 0.1, 0.25 wt%) Epoxy: Epon 828 Hardener: mPDA, DuPont (14.5/100)	CNT was dispersed in acetone, Ultrasonication for 6 h at room temperature; epoxy was pre-heated at 75⁰C. CNT in acetone solution was mixed with epoxy and ultrasonicator at 60⁰C for 2 h. Degassing in vacuum oven at 80⁰C for overnight. Curing agent was added and mixed. Curing at 80⁰C for 3 h and post curing at 150⁰ C for 2 h.	Surfactant treated CNT showed excellent stability for 48 h. Flexural strength and modulus increased up to 0.05 – 0.1 wt% and stabilized. Surfactant treated CNT showed better results than other CNTs – better dispersion and less agglomerates. T_g of surfactant treated CNT was higher than silane treated CNT. Raman graphs verified	Geng <i>et al.</i> , 2008

	Solvent: Acetone Surfactant: TritonX-100 with critical micelle concentration (CMC) at 0.2 mM at 25⁰C.		surface treatment that resulted in physical adsorption rather than disturbing CNT structure. Bridging effect between CNT and epoxy resulted in improved wettability than pristine CNT. Silane CNT showed lower flexural properties due to breakage of CNTs into smaller pieces. Pristine CNT (after impact test) – smooth fracture surface with small size, repetitive spatulate patterns Surfactant CNT (after impact) – rough and fluctuant morphology with large, elongated radial crack patterns	
8.	PMMA Monomer – methyl methacrylate (MMA) Hydroxyapatite (HA) in	HA filler was silanized using MPS in 90% methanol and 10% distilled water. pH was adjusted to 4.0 with acetic acid. Concentration of MPS (2, 4, 6, 8%) Water absorption test	Presence of silanol molecules introduced a hydrophobic layer on HA particle surface and the percentage of water uptake was slightly decreased. Fickian diffusion and Fick's	Tham <i>et al.</i> , 2010

	powder form. Silane: 3-methacryloxypropyltrimethoxy silane (MPS) with 98% purified contents.	conducted according to ASTM D570-98. Specimens were dried in vacuum oven at 70°C until constant weight was attained. Specimens were placed in DW at 27°C Simulated Body Fluid (SBF) was according to ISO 1567-2001. Specimens were placed in water bath at 37°C.	second law of diffusion is used to determine the diffusion parameter. Water diffuses into polymer matrices either through infiltration into free space i.e. micro-voids or specific molecular interaction controlled by available hydrogen bond at hydrophilic sites. Flexural modulus and strength of composites decreased initially but increased after a certain time period due to the post-chemical reaction during re-drying process. Presence of ions such as Na^+, K^{2+}, Cl^-, Ca^{2+} and $(\text{HCO}_3)^-$ led to formation of apatite on HA particle surface and especially $(\text{HCO}_3)^-$ induces increased rate of diffusion in sample by interacting with OH^- group. Decreased in flexural properties in wet-state after subjected to SBF for 1	

			month.	
9.	MWCNT: CVD, Acid (H₂ SO₄ :HNO₃) treated MWCNT Silane treated MWCNT with 2% 3-aminopropyltriethoxysilane Woven carbon fibre – WTR 3K with 0.27 mm thickness Epoxy – YD 115 (DGEBA) and G-A0533 (polyamidamine) curing agent	Silane treatment: 1.8 gm of O₂-CNT was dispersed in 2% silane solution, added to 300 ml ethanol: water. Stirred at 70⁰C for 4 h. Separated by filtration using distilled water and dried at 80⁰C for 12 h. 2 wt% MWCNT was used. Epoxy containing CNT was stirred in beaker at 700 rpm for 30 min with magnetic stirrer. 8 plies were cured in an autoclave.	Brittle nature for both acid and silane treated MWCNT composite. While, ductile behaviour of CF/epoxy composite. Silane MWCNT composite showed maximum increase in flexural modulus (5% for acid composite and 11% of CF/epoxy composite). Flexural strength of silane treated MWCNT increased (55% by CF/epoxy composite and 15% of acid CNT/epoxy composite). Wear properties of silane treated MWCNT were superior to those of acid treated. SEM images showed better dispersion of silane treated CNT along with better interfacial interaction. CNT resulted in less pull-out of nanotubes and CF was harmonized with epoxy matrix.	Kim <i>et al.</i> , 2011

			Lower coefficient of friction with f-CNT indicates improved dispersion and facilitates stronger interface bonding between CNT and epoxy matrix. Worn surface of carbon/epoxy composite exhibits exfoliation and cracks of epoxy matrix and breakage of CF. Silane CNT display smooth and shallow wear track.	
10.	CNT: MWCNT from Sunnao, China Fibre: glass fibre Matrix: Araldite LY5052 Hardener: Aradur 5052	MWCNTs purity was increased by washing with HCl at 100°C for 4 h. MWCNTs were then mixed in acetone by 1 h mechanical stirring followed by 1 h sonication. Epoxy resin was added to the dispersed solution by using stirrer for 15 min and 20 min of sonication. Mixture was heated above 65°C to remove the acetone. Hardener was added when mixture was at room	Addition of MWCNTs increased tensile strength and reduced fibre-matrix debonding. Pristine nanotubes are not so effective but, with interaction of silane treated glass fibres, interfacial reinforcing takes place which improves the toughness as well as tensile properties By adding 0.3 wt% tensile strength increased by 27%. FTIR analysis confirmed the Si-O-C linkage and SEM results showed good	Anas <i>et al.</i> , 2013

		temperature. Composites prepared using VARTM.	adhesion between fibres and matrix	
11.	XDCNT-NH ₂ (Diam: 9.5nm) consists of SWCNT and DWCNT along with carbon black and metallic impurities, concentration Of functional groups <4%. Epoxy: Epon 862 (DGEBF) Hardener: Epicure W (aromatic diamine), Ratio: 100:26.4 Fibre: Carbon fibre, 8-harness	XDCNT (0.15, 0.3, 0.4 wt%) mixed in resin using stirrer for 4-5 min. Mixture was put in sonicator for 1 h at 35% amplitude and 40s on/20s off cycle pulse mode. Mixture was kept in cooling bath. Mixture was further passed through three-roll mill to improve dispersion of XD-CNTs. Mixture was mixed with curing agent using a mechanical mixer Degassed in vacuum oven at 70 ⁰ C for 30 min. CF was stacked into 11 layers while maintaining parallel orientation. Two curing cycles: 121 ⁰ C for 2 h and 177 ⁰ C for 2 h and then allowed to cool. Post curing done at 177 ⁰ C for 2 h.	Mixing epoxy and AMWCNT results in interfacial reaction creating a cross-linking b/w amine and epoxide groups. Cracks are not able to propagate in nanocomposites through a CNT. Large volume of pull-out nanotubes are obs. And slows down crack propagation and changes its path. In ILSS test, failure occurs due to a combination of Interlaminar shear cracking, micro buckling, indentation and fibre rupture. Silane treatment of CF was done to make a durable bond between fibre and matrix. Once a silane is covalently bonded to fibre it allows wide range of chemical reactions with epoxy and amine group on CNT. Covalent bonding increases	Hossain <i>et al.</i> , 2014

	satin weave Silane: GPS		interfacial bonding and thus improves ILSS. Storage modulus increases by 17.22% at 0.3 wt% XDCNT and loss modulus also increased for the same concentration. However, storage modulus decreased above 120⁰C due to easier movement of polymer chain. T_g also increases for 0.3 wt%. At 0.4 wt% agglomerates are present that result in lowering its properties, interfacial adhesion b/w nano-fillers and matrix is lower and molecular mobility is higher. f-CNTs provide better dimensional stability. SEM results: At 0.3 wt% it showed only matrix cracking (increase in ILSS) At 0.15 and 0.4 wt% combination of delamination and cracking at matrix.	

			High concentration of CNT could result in high viscosity of resin and cause poor wetting during laminate fabrication and cause poor adhesion b/w fibre and matrix. Presence of amino groups on XDCNTs surface promotes good adhesion b/w CF and epoxy matrix.	
12.	E-Glass fibre: average diameter 18 μ meter (without sizing) MWCNT: >90%, length 1.5 μm, diameter: 10nm (Belgium) Silane agent: APS, 98% Epoxy Resin: DGEBA,	GFs were chemically treated with a basic piranha solution to purify fibres and increase the no. of silanol groups on surface by hydrolysis of siloxane network APS treatment (1%) in extra dry toluene. Fibres were heated at 80⁰C for 24 h in inert atm. After cooling fibres were removed and cleaned several times with toluene, acetone, ethanol and water to remove any traces of physically absorbed silane. MWCNT were functionalized with –COOH	TEM images showed that f-MWNT acid treatment generated surface defects and no smooth surface of the outer wall was observed XPS results showed increase in amount of nitrogen on sample surface due to silane treatment of GF. SEM images showed neat and smooth surface after basic piranha treatment due to possible hydrolysis of siloxane bonds. APS treated GF showed mountain-like topography due to the condensation of silanes on surface of GF.	Tzounis <i>et al.</i> , 2014

	EPR L20 Hardener: amine, EPH960 (100:34)	group and grafted onto GF surface	Grafted CNT on GF showed highest interfacial adhesion strength 65.4 MPa with increase of 48% as compared to GF-APS. (A plausible explanation is that epoxy monomer inter-diffuses through CNT grafted network and chemically interacts with both amine groups of GF via nucleophilic rings opening reaction, as well as with carboxyl groups of MWNT via esterification). It results in improved load transfer from matrix to nanotubes and causes overall improvement in IFSS. SEM images showed cohesive failure since matrix material was observed on the fibres after pull-out process. Nanoscale roughness can further introduce mechanical interlocking mechanism seen in more grafted MWNT on GF.	
13.	Fibres:	0.05 and 0.1 wt% CNT	Both grafting onto fibres and	Yu B <i>et</i>

HexTOW IM2C carbon fibres Matrix: Epoxy, Epilam 5015 – mixture of Bisphenol F and Bisphenol – A Hardener: Epilam 5015 – polyoxyprop ylenediamine Silane: 3- glycidoxyp ropyl tri- methoxysil ane CNT: NC7000 MWCNT, Nanocyl, Belgium, D: 9.5nm, L: 1.5 µm	content was added into solvent of ethanol and water and then ultrasonicated for 30 min MWCNTs were oxidized prior to their dispersion. Silane agent was then added into the solution as mentioned above Carbon fibres were soaked in silane coupling agent (with or without MWCNTs) for several minutes followed by natural dry. Incorporation of MWCNT into resin: CNTs was added into acetone prior to ultrasonication for 30 min using sonicator, mixture was then processed using homogenizer at speed of 15000 rpm for 30 min, the mixture was then added into epoxy resin – homogenized for 1.5h and then mechanically stirred for 4h at 55°C to remove the solvent completely.	addition in resin improved the interfacial bonding as compared to control sample. IFSS increased by 26.3% by incorporating 0.05 wt% MWCNT into silane coating on surface of carbon fibre whereas, it increased by 18.1 % when added into epoxy resin Chemical bonding introduced by silane coupling agent is considered as the predominant role in enhancing the interphase. The formed silane coating provides a strong connection between as-received CF and epoxy matrix. High CNT concentration is possible for grafting onto the fibre surface whereas, for dispersion in resin it will cause agglomeration and resin impregnation. Volume fraction of 0.05 wt% CNTs when dispersed in silane solution is 18 times higher than when CNT was	<i>al.</i> , 2014

			dispersed in epoxy resin (0.1 wt%)	
14.	Fibres: E-glass CNTs: MWCNT, purity > 95%, D: 5-10nm, L: 1-6 µm	MWCNTs were oxidized using a solution of H₂SO₄/HNO₃. This generates hydroxyl and carboxyl groups on CNTs walls and ends MWCNTs were coated onto as-received glass fibres as well as onto fibres whose sizing was removed	Homogenous deposition of oxidized MWCNTs over glass fibres was achieved at macro and micro-scales when glass fibre sizing was not removed If the coating is removed, it results in poor interaction with the MWCNT FTIR and XPS spectra provide evidence that the hydroxyl and carboxyl groups of oxidized MWCNTs react with oxygen containing functional groups on the glass fibre coating, forming hydrogen bonding and through epoxy ring opening. Hydrogen bonding and ester formation between functional groups of MWCNT and silane contained in coating was also possible	Ku-Herrera <i>et al.</i> , 2015

2.3 Hygrothermal aging of GFRP composites

Hygrothermal aging is referred to as the degradation of the mechanical properties of the polymer composite when subjected to a mixture of moisture and temperature. The changes observed in the mechanical properties of the composite are either reversible or irreversible or a combination of both depending upon the temperature and the exposed time.

The chemical changes occurring in the composites results in damages such as fibre breakage, matrix cracking and debonding of fibre/matrix interface causing permanent change in the mechanical properties of FRP composites.

Chateauminois *et al.*, (1993) studied the static fatigue behavior of hygrothermally aged unidirectional GFRP composites and the failure mechanisms associated with fatigue damage were investigated under three-point flexural loading. Depending on the aging temperature, two failure modes were observed: fibre micro buckling on the compression side or progressive cracking on the tensile side. Micro buckling was related to the reversible plasticization of the epoxy matrix by moisture ingress and the cracking on the tensile side was attributed to the irreversible weakening of the fibres and the interface at higher aging temperatures.

Iglesias *et al.*, (2002) studied the influence of different aminosilanes fibre coating on the strength of epoxy-based composite materials by using an easy fractographic test. A new method was also incorporated to gain information on molecular level at the interface by using fluorescence molecules. The experimental results revealed that the mechanical properties of GFRP materials is strongly dependent on the coupling agent. Crosslinking density and rigidity increases as the accessibility of the functional groups of the coupling layer increases. In addition, the interpenetrating adhesion mechanism seems to be the most important that affects the adhesion and subsequently the interfacial strength. It was observed that silanized glass fibres have lower rigidity when equilibrium water content is reached. Also, plasticization of matrix at the interface occurs due to hydrolyzed silane residues and water molecules. Further, the hydrolysis rate of the glass-silane siloxane linkages, Si-O-Si is greater than that of silane-silane linkages, Si-O-Si.

Raghavendra *et al.*, (2004) GFRP woven fabric composite material were tested to determine tensile, compressive and in-plane shear strength under both room temperature and hot-wet conditions. Prior to testing, hot-wet specimens were hygrothermally aged in an environment

chamber, maintained at 71°C and 85 % relative humidity (RH) until moisture absorption of about 1 wt% was attained. For hot-wet tests, a split type environmental chamber was fixed to the machine which was also maintained at 71°C and 85% RH. The test data obtained was statistically analyzed to determine mean strength of the specimen. The ultimate tensile strength was reduced by 11% in both conditions and 18% reduction was also observed in the compressive strength of the specimen. Presence of moisture in the epoxy matrix, in the fibre-matrix interface and the chemical attack of moisture on the glass fibres were considered as the main reasons for reduced strength of GFRP material in hot-wet condition.

Botelho *et al.*, (2006) studied about the environmental factors, such as humidity and temperature, that can limit the applications of composites by deteriorating the mechanical properties over a period of time. The degradation of composites due to environmental effects is mainly caused by chemical and/or physical damages in the polymer matrix, loss of adhesion at the fibre/matrix interface, and/or reduction of fibre strength and stiffness. In this work, the influence of moisture in shear properties of carbon fibre/epoxy composites (laminates [0/0]s and [0/90]s) have been investigated. Results for laminates [0/0]s and [0/90]s, after hygrothermal conditioning, exhibited a reduction of 21% and 18% in the interlaminar shear strength, respectively, when compared to the unconditioned specimen. Shear modulus showed a reduction of 14.1% and 17.6% for [0/0]s and [0/90]s, respectively, when compared to the unconditioned specimen.

Brun *et al.*, (2007) studied the hygrothermal conditioning of an DGEBA based epoxy resin filled with silica flour and cured with an anhydrid acid. The filler content was 60 % by weight. The samples were then conditioned in a climatic chamber at 80°C under 80% RH. The results indicated that the water intake of the unfilled samples was 1.5% after 5 days whereas the filled samples showed not much water intake. Thermogravimetric analysis showed degradation of filled samples after a period of 50 days which was not observed in unfilled samples. Lastly, decrease in elastic modulus and the glass transition temperature was observed to be more in unfilled samples as compared to the filled samples. After 50 days of conditioning, there was a shift in the glass transition temperatures for both the unfilled and filled samples.

Aldajah *et al.*, (2009) studied the impact of sea and tap water exposure on the durability of GFRP laminates. Specifically, E-glass polyester resin composite laminates were prepared by hand lay-up technique. The specimens were divided into two sections: symmetric and anti-symmetric.

The seawater was taken from Gulf of Arab and tap water from the tap of United Arab Emirates University. In general, the study stated that seawater and tap water have a negative impact on the durability of the laminates. Symmetric laminates lost about 53% of their flexural stiffness during the first 500h of exposure and it kept on decreasing with aging time but, at a very slow rate. Similarly, anti-symmetric laminates lost only 23% of its stiffness for first 500h. Overall, symmetric laminates lost approximately 60% of flexural modulus while anti-symmetric lost 28% after 2000h of exposure time. SEM images revealed weak adhesion between the fibres and the matrix which possibly caused significant reduction in the modulus. Besides this, the polymer matrix got deteriorated with the water absorption.

Jiang *et al.*, (2012) studied the moisture diffusion process in pultruded FRP composites of bridge decks when exposed to the vapour environmental aging condition as well as water immersed condition at temperatures of 20°C and 40°C respectively. After a short-term (250 days) aging duration, the moisture weight gain curves as a function of time were obtained. Comparing with the vapour conditions, FRP composites immersed in water resulted in much higher moisture uptake levels, around 3% of the initial self-weight. The obtained results indicated that high temperature can speed up the moisture diffusion rate, and the moisture equilibrium contents were mainly governed by the humidity of aging environment. Large portion of polymer relaxation was evident from the experimental data in the aging condition of 20°C-water and 40°C-water. Moisture desorption tests confirmed that, for the aging conditions of 40°C-96% relative humidity (RH) and 40°C-water, mass loss of FRP composites took place.

Prolongo *et al.*, (2012) epoxy resin composites with amino functionalized MWCNT and carbon nanofibres. A comparative study was carried out among the two nano-fillers. It was determined that the addition of nanofiller induces significant decrease of diffusion coefficient (20-30%) and its higher for CNT composites as they create barrier on epoxy matrix and also due to chemical linkage between epoxy and AMWCNT. Barrier properties of CNT are higher than CNF due to its high surface area. Nano-fillers have hydrophobic behavior while neat resin has hydrophilic behavior. T_g increases for composites reinforced with CNF than neat resin and T_g decreases for CNT since AMWCNT leads to a non-stoichiometric balance between epoxy and amino groups, thus inhibition of cross linking reaction. However, water uptake mechanism does not change with addition of nano-fillers. A decrease in water absorption and diffusion coefficient for

composites reinforced with A-MWCNT. The water absorption induces plasticization of the resin and improvement of post curing reaction. Finally, the influence of water uptake on the mechanical properties confirms the presence of two types of absorbed water molecules: Types I and II bound water. First the mechanical strength falls because of plasticization effect, thus reducing T_g and mechanical properties. Then, after saturation, a recovery of mechanical properties is registered due to the formation of a secondary crosslink network with hydrophilic groups of epoxy. 0.25% CNT shows higher mechanical properties and increase in strength is observed. Pulled out of CNTs confirm the presence of strong interaction between nanotube and epoxy matrix due to presence of amino groups.

Rao et al., (2012) studied the effect of GFRP composites when exposed to different water salinity at different temperatures and different exposure periods. Glass fibre laminates were prepared using resin transfer moulding process with the specimen dimension of 250x30x8mm. Some specimens exposed in water at room temperature for a period of 6 months. While some of the specimens were exposed to water bath and salt bath at 45°C for 60 days. The results after carrying out the three point bending test on the specimens are:

- Flexural strength decreases 26-70% when exposed in water bath and 29-74% in seawater for 2 months at 45°C.
- 25-50% decrease in flexural strength when exposed at room temperature for a period of 6 months

Moreover, the glass fibre materials were found to absorb more moisture which reduced the mechanical properties significantly. In addition, it was also noticed that the hygrothermal aging at elevated temperature resulted in greater strength degradation when exposed in salt water as compared to simple water.

Pe´rez-Pacheco et al., (2013) investigated the mechanical properties and failure modes of carbon fibre/epoxy (CRFE) unidirectional laminated composite that were exposed to a humid environment. The composites were exposed to three different humidity conditions i.e. 25, 55 and 95% at constant temperature of 25°C. Potassium acetate and magnesium nitrate hexahydrate were used for the 25 % RH and 55 %RH, respectively. The 95 % RH was achieved by placing a pan with natural water inside the chamber. It was observed that the moisture absorption rate was high at the beginning of the exposure of the samples, especially during the first 20 days for 25 and

55% RH; afterward, the absorption rate slowly decreased until 90 days of exposure and then it stabilized to a maximum of 1 %. Only for the 95 % RH environment, the absorption rate rapidly increased during the first 20 days, and then it stabilized to a moisture gain of 2 %, after 90 days.

The plasticization, swelling stresses and any epoxy degradation due to hydrolysis will contribute to the matrix failure mechanisms. It was observed that the tensile strength of laminates made with the silane coupling agents showed a decrease but after a moisture uptake of approximately 0.45% remained constant. The effect of the absorbed moisture on the mechanical behavior of the laminated composites was also studied by detecting the acoustic emission (AE) signals, while conducting the tensile test. The AE technique showed that the untreated carbon fibre failure mode was a result of fibre-matrix interfacial failure, whereas the silane treated CFRE laminate showed matrix failure followed by fibre failure without any fibre-matrix debonding, for moisture contents up to 1.89 %.

The literature review on polymer composites subjected to hygrothermal loading conditions has been summarized in Table 2.3, in a chronological order.

Table 2.3: Summary of literature review related to polymer composites subjected to hygrothermal loading

S.No	Material	Processing	Key results	Reference
1.	L1007 epoxy resin – flexibilised single polymer (Bisphenol A) Woven carbon, woven glass and woven polyester fibres. Hardener: polyoxypropylene	Laminates were cured for 48 h at ambient temperature and pressure, and post-cured for 16 h at 60°C. Natural sea water was collected from Poole Harbour, Dorset. Baths were maintained at 20 ± 0.5°C and 10 ± 0.5°C and three specimens were	Used Fick's law of diffusion to calculate the diffusion rate (D). Rate of uptake of moisture and D depends on temperature was confirmed. For all composites, values of D were greater at 20°C than at 10°C. Navy GRP showed least	Adams and Singh, 1995

	diamine Navy GRP = isophthalic polyester resin with woven GF.	immersed in each bath for 3 months until total time of 15 months. 3 samples of unreinforced resin were soaked at 20⁰C.	uptake of water and D was least affected by change in temperature. And also followed Fick's Law as diffusion was the primary mechanism for water uptake. At 20⁰C both GF and polyester fibre reached a peak mass and decreased in weight rather than reaching a saturation level, possibly due to some of the elements of composite that were leaching out into water. Epoxide composites absorbed more water in seawater conditions. Absorbed water led to loss of stiffness and increase in load transfer at both 10⁰C and 20⁰C. Dynamic properties of the epoxide composites changed when exposed at higher temperature. Moisture uptake was not simply due to diffusion of	

			water but also due to osmotic process. Osmotic effect causes more moisture to be absorbed quickly and reaches higher saturation content when immersed in tap water and while absorption is even greater in DW. More water was absorbed by glass fibre interface due to capillary action whereas in polyester fibre it was absorbed by fibres. Carbon fibre composites were least affected. T_g decreases due to absorbed moisture and for higher temperature more decrease is observed. DW absorbed more water than SW since DW is free of any solute ions and if any salt ions are present in the material they will tend to move from regions of low concentration into the	

			material to dilute the solution. Effective modulus was higher at 10⁰C than 20⁰C. Modulus dropped to 80% of initial value for carbon fibre. Modulus showed sharp drop initially but became constant after 55 days.	
2.	Resins: orthophthalic polyester (115 PA), isophthalic polyester (491 PA), vinyl ester (Atlac 580) and epoxy (SR1500 – DGEBA) E-glass fibre Amine hardener (2505) 6 layers were used and total thickness of laminate is 4 mm	Composite panels were produced by hand lay-up in a temperature of 20⁰C and humidity of 50% RH. 6 layers of E-glass fibre in 0⁰/90⁰. Post-curing at 90⁰C for 6 h 18 months immersion time was calculated to simulate a 12 year service life. Baths with distilled water (DW) and natural seawater (SW) (from Brest Estuary) were kept at 50⁰C. Samples were cut and dried for 48 h at 50⁰C. They were weighed and then placed in water.	Distilled water aging differs significantly from seawater aging in terms of weight gain however in terms of shear property changes it's similar. Rule of thumb used: 10⁰C rise in temperature causes a doubling of diffusion rate. Epoxy shows a plateau region within 6 months at 20⁰C while weight keeps on increasing after 18 months but stabilizes after 42 months. Desorption rate at 20⁰C in SW are very similar to	Davies <i>et al.</i> , 2001

		After aging specimens were wiped, immediately tested in wet conditions to reveal closest to in-service conditions.	50⁰C in SW. Weight gain is more in case of DW than SW due to the presence of salt ions that block diffusion passages. Fibre-matrix surface is more susceptible to DW than SW. Permanent changes occur in polyester composites after 18 months whereas epoxy and vinylester composites are less affected and largely recovered after drying. Tensile strength decreases by 20% for polyester, 40% for epoxy composite.	
3.	E-glass plain woven fabric with a weight of 0.329 kg/m². Glass/Polyester, Carbon/Polyester, Glass/Vinyl Ester and Carbon/Vinyl	Hand layup method. Specimen's size: 120 x 120 mm with thickness of 1.6, 3.0 or 4.2 mm. Laminate curing both at room temperature and high temperature. Edges were sealed with	Glass polyester and glass/vinylester composites showed higher mass gain than their respective counterparts reinforced with carbon fibres. Polyester based chemicals are less stable	Kootsooko s and Mouritz, 2004

	Ester composites.	resin matrix and immersed in sea-water. Salinity of 2.9% and temperature of $30 \pm 0.5^{\circ}\text{C}$ for two years (changed water monthly).	in sea water than vinylester based composites because polyester resin undergoes hydrolysis resulting in leaching out of ester species with hydroxyl group. Flexural modulus decreased by 30% for vinyl-ester based composites and approximately 20% for polyester based composites. Flexural strength decreased by 40-50% for vinyl based composites and 20-40% for polyester based composites. No significant change in mode I Interlaminar fracture toughness.	
4.	Carbon/Epoxy laminates (64% fibre by volume).	Autoclave Forming.	Compressive tests in the hydrostatic pressure environment indicated increase in compressive elastic modulus, fracture strength and fracture	Rhee <i>et al.</i> , 2004

			strain with increase in pressure up to 270 MPa. End-crushing and delamination cracks were fracture modes at all pressure levels.	
5.	IM7 carbon fibre mixed with Epon 8552 resin	Samples divided into 3 families: Kept at room condition for 9 weeks, humidity controlled chamber (ASTM D5229 M-04 [3], Procedure B) at 80⁰C and 95% RH and lastly in salty spray chamber according to ASTM 117 -03 [2] for 9 weeks. 5 w/w% in 95 distilled water parts with a pH of 6.5 – 7.2 at 35⁰C.	Compression tests at two temperatures i.e. 22⁰C and 82⁰C. 8% decrease in compressive strength for samples tested at room temperature and subjected to salt water conditions. 18.5% decrease in compressive strength at high temperature under salt water conditions. 25.7% decrease for samples tested at high temperature and moisture controlled conditions. Hence, high temperature of test reduces the compressive strength due to degradation of polymer matrix and/or fibre matrix	Cunha <i>et al.</i> , 2008

			interface.	
6.	T700 carbon fibre with 'F' sizing agent with vinylester (VE D411) resin, AS4 E-glass fibre with silane sizing. Polymer matrix composites for naval applications.	4-ply laminates were prepared using VARTM at room temperature and cured for 24 h. Thickness after curing was 1.2 mm. Specimens were immersed in distilled water at 40⁰C and seawater at 60⁰C.	E-glass fibres exposed to sea water at 60⁰C lost 50% of their strength after 2 days as compared to carbon fibres. EP absorbed much more water than neat vinyl ester. Tensile and flexural strength of epoxy composite were reduced by about 60% and 30%, respectively. On the other hand, tensile and flexural strength of vinylester composite were reduced by ~40 and 45% respectively. Fibre breaks and fibre/matrix debonding was observed in optical transmission microscopy.	Ramirez <i>et al.</i> , 2008
7.	T700 Carbon stitch bonded fabric with a weight of 634 g/m². Vinylester –	VARTM process. Specimen size: 60 x 90 x 2.54 cm Specimens were soaked in	Fracture toughness is reduced by 30% for sea-water simulated conditions. The delamination crack	Siriruk <i>et al.</i> , 2009

	DERAKANE 510A-40 (Dow Chemical's) Divynicel PVC Foam as Core.	simulated sea water using natural coarse sea salt at a controlled temperature of 40 ⁰ C for 3 months.	propagates close to the interface in the wet case, while it stays within the foam in the dry case.	
8.	Unidirectional GFRP composite (52% fibre by volume) Unidirectional glass/polyurethane composite (58% by fibre volume)	GFRP laminate fabricated by continuous lamination process. Glass/polyurethane laminate fabricated by pultrusion process. Thickness reduced from 6 to 3 mm by grinding technique Specimens immersed in seawater from Arabian Gulf at 23 ⁰ C and 65 ⁰ C for 3, 6, 12 months.	Specimens weighed before submission and after submission in seawater at 30 days interval. High temperature activates the diffusion of water molecules through the composites. Absorption of seawater increased gradually with time and higher temperature in both composite materials. X-ray spectra revealed no permeation of seawater ions into the matrix or fibre/matrix interface after 1 year of exposure. 25% reduction in tensile strength of glass/polyurethane composites subjected to seawater conditions,	Mourad <i>et al.</i> , 2010

			while no effect on GFRP composite. At room temperature hydrolysis causes swelling in matrix that may lead to improved mechanical adhesion between the fibre and the matrix. Glass fibres showed no damage when exposed to seawater conditions for 1 year at room temperature however failed in brittle mode at high temperature. In GFRP composite mode of failure changes from brittle matrix and ductile fibre to ductile matrix and brittle fibre.	
9.	PMMA Monomer – methyl methacrylate (MMA) Hydroxyapatite (HA) in powder form.	HA filler was silanized using MPS in 90% methanol and 10% distilled water. pH was adjusted to 4.0 with acetic acid. Concentration of MPS (2, 4, 6, 8%) Water absorption test	Presence of silanol molecules introduced a hydrophobic layer on HA particle surface and the percentage of water uptake was slightly decreased. Fickian diffusion and	Tham <i>et al.</i> , 2010

	Silane: 3-methacryloxypropyltrimethoxy silane (MPS) with 98% purified contents.	conducted acc to ASTM D570-98. Specimens were dried in vacuum oven at 70⁰C until constant weight was attained. Specimens were placed in DW at 27⁰C Simulated Body Fluid (SBF) was acc. ISO 1567-2001. Specimens were placed in water bath at 37⁰C.	Fick's second law of diffusion is used to determine the diffusion parameter. Water diffuses into polymer matrices either through infiltration into free space i.e. microvoids or specific molecular interaction controlled by available hydrogen bond at hydrophilic sites. Flexural modulus and strength of composites decrease initially but increase after a certain time period due to the post-chemical reaction during re-drying process. Presence of ions such as Na⁺, K²⁺, Cl⁻, Ca²⁺ and (HCO₃)⁻ led to formation of apatite on HA particle surface and especially (HCO₃)⁻ induces increased rate of diffusion in sample by interacting with OH⁻ group.	

			Decrease in flexural properties in wet-state after subjected to SBF for 1 month.	
10.	Polyester resin and glass/polyester laminated composite. PMEC 50 to initiate the hardening reaction.	Composites are prepared by hand lay-up process and stacking sequence is in form [mat300/mat450/mat600/2 [mat600/roving500/mat600]]. Curing cycle was 24 h at room temperature and post curing y 16 h at 40⁰C. Samples were immersed in natural seawater at 22⁰,40⁰ and 60⁰C.	Decrease in elastic modulus with increase in temperature of aging i.e. decrease of 20% at 60⁰C. Tensile strength improved, gain in ductility for the resin composite immersed in seawater at 22⁰C. At low temperatures, fibres and fibre-matrix did not have a mass uptake whereas at high temperature absorption was recorded. Strength and toughness of materials was reduced due to seawater immersion (chemical degradation).	Laoubi <i>et al.</i> , 2012
11.	Epoxy: Bisphenol A and Bisphenol F with 2,3 – epoxypopyl	Seawater (SW) conditions were prepared according To ASTM D1141. De-mineralized water	Equilibrium moisture content reached after 57 days, 2.18% for SW and 2.31% for DW. It is	Zafar <i>et al.</i> , 2012

	diluents Hardener: IPDA Ratio: 100:35 CF: HM35 (without sizing) Seawater and distilled water	(DW) was taken. Both DW and SW were kept at ambient temperature and immersed from 12 days till 300 days.	higher for DW specimens than SW (because presence of salt in SW reduces the activity of water molecules and also salt particles are less readily absorbed than water. Salt particles get deposited on the surface and inhibit water absorption. Diffusion coefficient (D) for EP in SW is 7.89×10^{-14} and for DW is 8.4×10^{-14}. Presence of hydrophilic group in epoxy due to OH group can also react with water molecules to form weak hydrogen bonds. This absorbed water acts as a plasticizer by Increase mobility of chain and decreases T_g. Resin properties that are degraded can be restored by removing the matrix. Tensile strength decreased by 30% for SW 300 days, Young's	

			modulus by 10% whereas 7.5% for DW300. 28% in final elongation of the moisture samples compared to dry samples. Fibres in dry samples are in compression while wet ones are in tension. Swelling due to water uptake has large influence on samples in DW than SW. Chemical degradation is a result of hydrolysis of bonds at interface and is a function of environment temperature and pH value. Mechanical degradation is due to matrix swelling causing stress large enough to pull out the matrix from the fibre.	
12.	MWCNT – 90% purity, diameter – 9.5 nm T300 carbon plain weave (Sigmatex)	15 layers of carbon fibre laminates were prepared using hand lay-up technique. Panels were cured under vacuum for 15	MWCNT do not have significant effect on the corrosion and mass loss rate. Conventional hybrid	Arronche <i>et al.</i>, 2013

	Epoxy Resin – bisphenol A Hardener – 117LV and 237	h at room temperature followed by 8 h at 22⁰C. 0.5 wt% (1.95g) of MWCNT was added to 200 mL of acetone, sonicated for 60 min at 25⁰C. 300g of epoxy resin was sonicated for 30 min at same temperature. Acetone was evaporated by placing in a hot-plate at 50⁰C for 6 h. solution was cooled in an ice bath for 40 min and 90 g of hardener was added. Mixture was mixed manually for 5 min and degassed for 60 min to remove air bubbles. Samples immersed in electrolyte solution of 2 wt% NaCl aqueous at 40⁰C.	CFRP/steel joints and repairs may be sufficient to delay galvanic corrosion	
13.	Epoxy: CP230D (DGEBA) Hardener: CP230H (amidoamine) Fibre: E-Glass (CSM) specific	Epoxy and hardener were mixed in 10:6 (w/w%) CNT (0.5 – 2.0 wt%) was added to mix using ultrasonication and mechanical stirring process Poured onto 4 layers of GF	Flexural modulus and strength increases up to 1.0 wt% CNT and decreased on further addition of CNT. Larger agglomerates were visible at 1.5 and 2.0 wt%.	Zulfi <i>et al.</i>, 2013

	gravity = 2.6 CNT: MWCNT (aspect ratio = 500)	by hand lay-up technique. Curing in an oven at 110⁰C for 3 h. Water absorption acc to ASTM D570-98. Samples were dried at 80⁰C in vacuum and immersed in water bath filled with water at 30⁰C, 60⁰C, 90⁰C. D was calculated using Fick's law and Arrhenius equation.	Impact strength increases up to 1.0 wt% (i.e. 78%) CNT (because CNT hindered and delayed the crack propagation through bridging mechanism). Fracture toughness also increases up to 1.0 wt% (due to bridging effect and large aspect ratio allows them to act as nanobridges between notch edges). Water uptake was high for CNT nanocomposites than GF/epoxy composite due to presence of hydrophilic groups on CNT. For water absorption, the saturation occurs after immersion of 12 months. Ea (activation energy) for MWCNT composite is lower than EP composite. i.e. water molecules need less energy to diffuse through CNT composites.	

			Kinetics of water absorption of Epoxy/GF/MWCNT composite followed Fick's Law.	
14.	Resin: Epoxy (Araldite LY-556) Hardener: aliphatic primary amine (HY-951) Fibres: Woven E-glass	18 layered structures were fabricated by hand lay-up. Test specimens were immersed in beakers containing seawater for 1,2, 3 and 4 weeks. After that time, samples were wiped dry and weighed to determine seawater ingress.	Moisture ingress is anomalous for seawater immersion Exposure for higher period in seawater still results in lower water absorption as compared to distilled water. With lapse of time, moisture absorption becomes Non-Fickian. It is attributed to development of micro cracks, delamination, debonding etc. as a result of the swelling of the matrix. ILSS value is significantly affected with increasing immersion time. Up-thermal shock is more harmful to the composite material as compared to	Chakraverty <i>et al.</i> , 2013

			down thermal shock. T_g depression is more visible under up-thermal shock as compared to under down thermal shock. The mode of failure was observed to be mainly fibre pull-out, fibre fragmentation and delamination.	
15.	Epoxy: DGEBA Hardener: TETA	8 different resin: hardener ratios were prepared. Samples were cast in plate-shaped open silicone molds. Samples were then soaked in distilled water	Weight gain due to water absorption increased with increasing amine (hardener) content, while diffusivity was lowered. The trend observed for these two parameters could be explained by the increase of free volume within the material, and by interactions caused by chain polarity and topology. A non-Fickian behavior was observed for all the samples prepared. The amine-rich systems have a more closed	Pereira and Almeida, 2016

			structure, since excess of amines will promote opening of the all available epoxy rings and will result in a highly cross-linked structure, leading to a drop in diffusivity rate and increase in volume fraction.	

2.4 Health monitoring of FRPs using ultrasonic guided waves

Structural health monitoring is done to accurately characterize the damage and predict the remaining life of the composites to minimize the operating costs and risks associated. Out of many commonly used Non-destructive techniques for health monitoring, ultrasonic guided waves (UGW) have started being used by researchers as it offers the advantage of monitoring large areas and also provide complete information about location, severity and the type of the damage by exploiting different modes. Guided waves are highly sensitive to structural damages and to the material in-homogeneities even when they are small in size or just lie beneath the surface. It is due to their excellent properties such as longer propagation, lower attenuation, economical implementation, ease of generation and acquisition of signals as compared to ultrasonic bulk waves that these are used by researchers. Various recent works in which UGW have been used for damage monitoring in FRPs is outlined below.

Kishore *et al.*,(2000) developed a two-dimensional finite element model with absorbing boundary conditions to investigate the scattering of ultrasonic waves in infinite isotropic solids. The model was capable of showing a complex mode-conversion, when a short duration sinusoidal pulse interacted with a flaw like; narrow crack-like defects, cylindrical and spherical holes of size equal to the wavelength of the incident wave. Results in the form of snapshots and scattering cross-sections provided good understanding wave–flaw interaction, especially mode-conversion of the incident field due to interaction with flaw.

Kundu et al.,(2001) studied the importance of near Lamb mode imaging of multilayered composite plates. Different Lamb modes generate various stress levels in different layers, so all Lamb modes are not equally sensitive to internal defects of various layers. In this paper it was investigated how by fine-tuning the frequency and striking angle of the incident beam in the neighborhood of a Lamb mode one can separately detect internal defects in layers of mirror symmetry in the upper and lower halves of a plate. Figure 2.1 shows the internal defects in five layers of composite plate. The incident angle and the signal frequency should be such that they are close to Lamb mode but not exactly on Lamb mode.

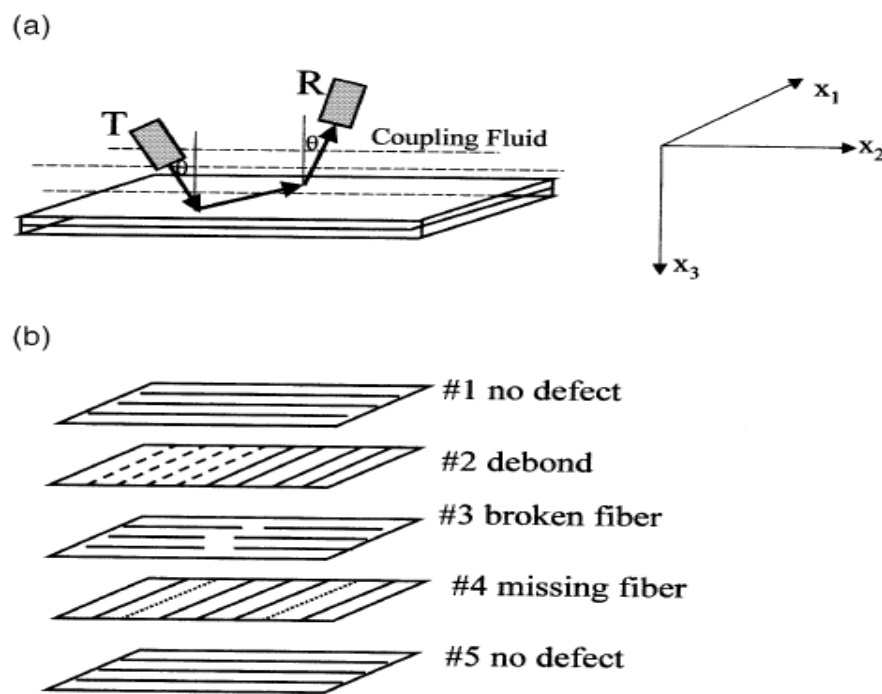


Figure 2.1(a) Relative orientation of transmitter, receiver and plate specimen, (b) schematic diagram of the internal defects in five layers of the composite plates specimen [Source: Kundu et al., 2001]

Kessler et al.,(2002) presented study on *in-situ* damage detection of composite materials using Lamb wave techniques to quasi-isotropic graphite/epoxy test specimens containing delamination, transverse ply cracks and through-holes defects. Linear wave scans were performed on narrow laminated specimens and sandwich beams with various cores by monitoring the transmitted waves with piezoceramic sensors. The time of flight of a Lamb wave pulse between an actuator

and sensor was determined. Lamb wave techniques provide the possibility of determining damage location due to their local response nature. The disadvantage of Lamb wave methods is that they require an active driving mechanism to propagate the waves, and the resulting data can be more complicated to interpret than for many other techniques. Overall however, Lamb wave methods have been found to be effective for the in situ determination of the presence and severity of damage in composite materials.

Prasad *et al.*,(2004) presented a study on structural health monitoring of composite structures using Lamb wave tomography. The study presents the possibility of constructing tomograms from a network of sensors generating and sensing Lamb waves in thin, multi-layered, anisotropic composite plates. Improved tomograms are seen due to the following reasons:

- When the anisotropic and attentive characteristics of composite plates are accounted for by using the newly identified energy of the earliest Lamb wave signals as the reconstruction parameter
- Modifying the sensor configuration from conventional geometries (and thereby also optimizing the number of sensors) and
- Normalizing the Lamb wave energy data of the defective sample with respect to that of the defect-free sample

Sensors were arranged in a modified cross-hole configuration. The energy of the early part of the Lamb waveform is an effective parameter for tomographic reconstruction. Narrow bandwidth transducers such as PZT crystals excited by tone burst signals were found to be more suitable than commercial transducers, which had larger bandwidths.

Experimental results indicate that in anisotropic composite laminates, the tomogram obtained from modified cross-hole configuration (with sensors on all four sides) distinguishes the defective region better, when compared to the tomogram obtained from the regular cross-hole configuration.

Demcenko *et al.*,(2005) discussed the application possibilities of air-coupled ultrasonic technique for investigation of the Lamb wave propagation in the composite material and the numerical simulations of the Lamb wave interaction with the delamination type defect were presented. The Lamb wave velocities were measured in delaminated and defect-free areas of the

composite material GLARE. The structure of the GLARE composite is shown in Figure 2.2. The delamination position influence on the Lamb wave propagation velocity is investigated experimentally and numerically. They concluded that the air-coupled ultrasonic measurement technique can be used for accurate investigation and testing of various types of the materials, but it is not suitable for the fundamental investigations of the wave's interactions with the non-homogeneities or defects in the structures.

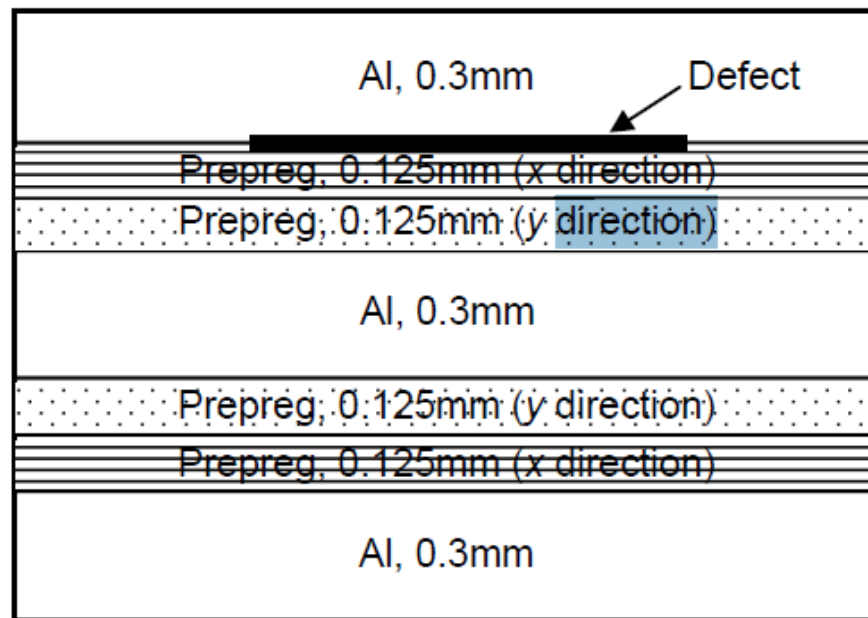


Figure 2.2 Structure of the GLARE3-3/2 composite and the position of the defect [Source: Demcenko *et al.*, 2005]

Wood & Loveday (2006) used guided wave for the inspection of cracks in glass fibre reinforced composites rods. Specially developed waveguide finite elements are used to determine the wave propagation characteristics of the rod. Conventional transient finite element modeling is performed in order to determine what effects cracks have on the passage of the induced waves, and therefore also on the eventual output signals. Additionally, the guided wave analysis allows for a better interpretation of measured signals, since modal velocities and dispersion characteristics are predicted. The presence of damage results in reflected signals and changes in the transmitted signals, both of which are quantifiable in terms of reflection and transmission coefficients. It has been shown that these coefficients can be defined and recorded in different

ways, but they can be used to quantify the extent of damage present in a sample, relative to undamaged samples. In conclusion, the experiments carried out have shown that the damage in the rod can be detected from its interactions with guided waves.

Rizzo *et al.*, (2010) presented application of hybrid laser/immersion transducer system for long range inspection of underwater structures. Elastic waves were generated in a submerged aluminum plate (1200 x 900 x 1.5875 mm) using pulsed laser. A pair of conventional immersion transducers was used to detect the propagating waves. Transmission of lowest order symmetric, anti-symmetric leaky Lamb modes and quasi-Scholte wave mode were studied. Time domain signal was processed using the Gabor Wavelet transform to obtain ultrasonic energy transmission coefficients. Two simulated damages, a rectangular notch (30 x 1 x 1 mm) and a circle (diameter 4mm and 1 mm depth), were machined on the specimen. Authors reported that the selected modes were significantly modified by the presence of these defects. Authors suggested using small lift off distance for Scholte mode because the amplitude of particle motion reduced significantly away from the interface. This work provided an effective non-contact approach to inspect underwater structures.

Pistone *et al.*, (2013) presented an automated non-contact damage detection technique for monitoring of immersed metallic plate by using leaky Lamb waves. Authors used hybrid setup comprising of laser-induced ultrasound exciters with array of immersion transducers as detectors. Time domain signal were processed to obtain damage-sensitive features and were subsequently used in a multivariate outlier analysis. Results were related to the simulated defects inflicted on the specimen. Finite element (FE) model was also developed to simulate the propagation of the guided waves in plate and pressure field in the liquid. A monitoring system for the automated inspection of immersed structures was designed by the authors and the repeatability of system was ensured by comparing the signals recorded at same point on inspection of the specimen many times. Signal processing algorithm adopted in this study was able to capture an artificial notch clearly and was partially able to detect a through-thickness hole that was as small as few millimeters. A dent and a simulated corrosion (plate thinning) were not detected probably due to their small size.

Sharma and Mukherjee (2014) describe a non-contact and non-invasive health monitoring strategy for submerged plate structures using guided waves. The structure under consideration is

immersed in water and subjected to longitudinal ultrasonic waves at specific angles of incidence using a cylindrical piezoelectric transducer where water acts as a coupling medium. Suitable ultrasonic guided wave modes with optimum scanning capabilities were generated and identified in submerged plate system. Finally, the propagation of selected modes through submerged notched plates was investigated which is beneficial in identifying damages in the submerged plate structures.

Sharma and Mukherjee (2015a) reported a non-contact, *in-situ* and non-destructive corrosion monitoring methodology for submerged plates using ultrasonic guided waves. Specific surface sensitive and core sensitive guided wave modes were utilized for monitoring plates undergoing accelerated impressed current corrosion in the presence of chlorides. A combination of the selected guided wave modes could effectively discern various corrosion mechanisms occurring in plates. Along with the ultrasonic signals, mass loss, stress–strain behavior and tensile strength of the plates at different stages of corrosion was also monitored and used to develop algebraic relationships amongst these parameters.

Sharma and Mukherjee (2015b) discusses about the application of ultrasonic guided waves as a structural health monitoring tool. Specific Lamb wave modes sensitive to near surface and sub-surface damages were identified in this study. Also, these modes were further utilized for non-contact scanning of the plates to identify the presence as well as extent of damage such as notches and corrosion. Effective combination of specific Lamb wave modes led to a comprehensive inspection of the submerged plate structures. Lastly, the data generated from scanning the plates was represented in the form of defect maps particularly, tomograms.

Pistone and Rizzo (2015) investigated various type of defect orientations introduced in an aluminum plate when submerged in water. The five defects that were identified are: 60 mm long transverse cut, 80 mm oblique notch, 6 mm circular dent, 10 mm through thickness hole and 40x40mm abraded area to simulate corrosion. On excitation, leaky Lamb wave mode, S_0 , was identified between 60-80 μ s. These waves represent quasi-Scholte wave and the bulk waves travelling in water. A_0 mode was not observed because most of wave energy was converted into quasi-Scholte wave. Interestingly, a decrease in cross-correlation coefficient was seen which is due to the presence of damage between the actuator and the defect. Similar behavior of the coefficient was also visible for all the defects. The signals were also processed to extract several

features in time, frequency and joint-frequency domain. Lastly, it was found that the array of immersion transducers and the signal processing technique was reliable as it showed reproducibility of results and the success rate of defect detection was close to 95%.

Table 2.4 summarizes the articles arranged in a chronological order and related to the use of ultrasonic guided waves for detecting defects in composite materials.

Table 2.4 : Summary of literature review related to polymer composites tested using UGW

S. No.	Material System	Methods used/ Methodology	Key Results	Reference
1.	Graphite-epoxy skin was 1 mm thick with sequence of [0/90/0]. Specimen was 150 x 200 mm. Delaminated area was rectangular (25x50mm) and circular (diameter = 25mm). The skin was bonded to Nomex honeycomb structure and epoxy was left for curing.	Variable angle beam transducers are used in which incident angle is changed in small increments to sweep through phase velocity. High amplitude -> mode travelling primarily in skin with very little alternation caused by epoxy and/or honeycomb. Characterizes that majority of energy is propagating through skin or represents a leaky wave confined to skin due to severe delamination b/w core and skin.	Increase in received signal amplitude between bonded area and delaminated area i.e. a leaky wave in the structure. 13dB difference was observed in reference to rectangular delamination at $v = 3900$ m/s. it implies that GW has desired displacement field that is sensitive to skin-core interface condition. Wave travelling is coupled strongly into the adhesive layer and Nomex honeycomb. Change in displacement	Hay <i>et al.</i> , 2003

		Low amplitude -> leaky wave mode coupled into the core. Measure of mode's sensitivity to the delamination at skin-core interface. Angle varied from 20^0 – 70^0 in 5^0 increments.	field also changes the sensitivity to the skin-core interface. Guided wave excited at 0.5 MHz showed superior sensitivity.	
2.	E-glass woven fabric L1000 – epoxy resin VE5195 – hardener	Specimens prepared using hand lay-up and thermally hardened at 50^0C for 24 hours Dimensions: 120x90x10 mm 8 measurement points on surface of specimen UT transmitter (1 MHz) with diameter of 13 mm using pulse-echo technique	Content of glass in a composite material causes an increase in velocity of the wave. Geometrical form of the reinforcement and resin type along with content of fibre influences the ultrasonic wave velocity. Pulse-echo technique is more convenient for determining the ultrasonic wave velocity in specimens with varying fibre content.	Wróbel <i>et al.</i> , 2006
3.	3 quasi-isotropic laminates with [0/+45/-45/90]_s lay-up were	3 delamination of each length 95 mm and widths of 40, 20 and 10 mm were induced.	The angles of the probes was set at 18^0 and used to excite and receive A_0 Lamb wave mode.	Ramadas <i>et al.</i> , 2011b

	prepared from carbon fibre reinforced polymer prepregs.	Air-coupled, non-contact ultrasonic probes were used which had a frequency of 200 kHz. Pitch-catch arrangement was employed for ultrasonic testing with a probe separation kept at 85 mm throughout the experiment.	When probe distance is equal to the delaminated area, Zone 2 did not exist because the probe unit traversed zero distance in this arrangement. Numerical B-scan revealed that the size of zones in B-scan depend on size of delamination in comparison with probe separation distance and probe diameter. In case of rectangular delamination, contour lines are straight because the width of delamination does not change with length. Size of zone 2 in D-scan expressed in terms of the length of the delamination and the probe diameter was used to estimate the length of delamination. Hence, the predicted values of the length of delamination in all 3	

			laminates were in good agreement with the actual values.	
4.	Specimen was made of carbon fibre reinforced plastic with a dimension of 250x50x2 mm (healthy). Two plates A and B were cut from the healthy plate having a rectangular and hole defect in the plate.	The test specimen was clamped at one end on cantilever support fixed on basement and a coupling fluid is used between transducers and test specimen for getting better results. Pitch-catch RF Test method was implemented having 10 kHz-4 MHz frequency. Point-contact sensors with 8mm diameter were used for transmittance and receiving the signal.	Specific Lamb wave mode, A_0, was generated by calibrating the ultrasonic set-up. There was a maximum rectification of error in case of specimen with through hole whereas the error rectification was minimum in the specimen with cut in it. Damaged specimen with through hole, the time appeared at the same phase and frequency, but was delayed by about 1μs due to the damage. Whereas, for the other damage the frequency got changed and also a large reduction in amplitude and varying change in phase occurred. The most effect on signal was observed for the cut defect as it had the	Ben <i>et al.</i> 2013

			smallest sensed voltage amplitude. The loss of energy in the damaged specimen is due to the dispersion caused by the micro-cracks within the laminate in the excitation of high-frequency local modes.	
5.	Unidirectional glass/epoxy laminate was fabricated using VARTM and had a thickness of 30mm.	A delamination was formed by placing a sheet of release film of specific dimension between 2nd and 3rd dry fibre layers. Once the sample was cured, the release film was pulled out thus, creating a true delamination in the sample. A pair of 200 kHz air coupled transducers along with Olympus 5077 pulser-receiver system was used to generate A_0 and S_0 Lamb wave modes. A 3-axis X-Y-Z scanner was used to	Rayleigh waves were excited at 14° for maximum amplitude. The primary Rayleigh wave upon interacting with the leading edge of delamination converts into Lamb wave in the delamination. Lamb wave mode experienced reflection and transmission at the trailing edge of the delamination resulting into convergence to Rayleigh wave. The presence of air path increased the time of flight values. An important application	Chakrapani and Dayal, 2014.

		facilitate B-scan capabilities.	of this study was that it could be used to determine the depth or thickness of delamination.	
6.	6 glass fibre sheets were reinforced with unsaturated orthophthalic polyester resin to form a laminate.	Samples were immersed in distilled water for 3, 6, 9, 12, 20, 40 and 100 days. Panametrics pulser-receiver system was used for ultrasonic measurement. A transducer G5KB-GE was used for the generation of ultrasonic guided waves while using honeybee wax as the coupling medium.	The mechanical tests results showed better properties for composite prepared using <i>in-situ</i> method as compared to other two step method adopted. Additionally, the T_g was higher by 10°C for this sample as compared to other samples. The measurement of the propagation speed of the longitudinal and transversal waves can be used for determining elastic modulus, shear modulus and poisons ratio. The phase velocity of Lamb waves is directly related to the mechanical properties of the composite.	Šturm <i>et al.</i> , 2015

			The non-destructive test results were in agreement with those obtained using DMA destructive tests.	
7.	Cross-ply E-glass fibre epoxy laminate with a stacking sequence of [0/90/90/0] Compression molding process was used to obtain planar plates of uniform thickness	Guided wave, namely, So mode, at a frequency of 200 kHz was generated Acoustic sensors were also were also integrated to develop a multi-functional NDT set-up.	The first conclusion of the study was that the developed multi NDT technique approach could characterize the damage of the composite material under uniaxial tensile tests. Guided waves were very sensitive to the damage that happened parallel to the loading direction. Additionally, acoustic sensors were able to detect signals coming from any direction and took into account all damage mechanisms from microscopic (matrix cracking, fibre breakage) to macroscopic (delamination) scales. Lastly, this study suggests that it is possible to effectively combine	Chaki <i>et al.</i> , 2015

			various NDT methods in order to validate or for a complete diagnosis of the health of the materials.	
8.	AS4/3502 graphite epoxy composite laminate was studied.	Air coupled ultrasonic transducer and laser Doppler vibrometer (LDV) set-up was used.	Snell's Law was found to relate the velocity of an incident bulk wave to the phase velocity of a generated Lamb wave mode. Group velocity found using time-of-flight Morlet wavelet transform (MWT) was in good agreement with the theoretical predictions. The proposed methodologies, Snell's Law and MWT were sensitive to the anisotropy of the composite laminates The proposed methodology is suitable for the detection of delamination in composite laminate which would be further useful for damage	Harb and Yuan, 2016

			detection in aerospace composite structures.	

2.5 Closing remarks

After the discovery of carbon nanotubes by S. Iijima in 1991, there has been a phenomenal growth in the synthesis of various composites using these carbon nanotubes. The literature review allowed gaining an insight about various synthesis techniques for improving the matrix properties for specific applications and needs only. In addition, the effects of dispersing carbon nanotube in polymer composites on their chemistry, mechanical and thermal properties have been studied thoroughly. Survey indicates that a new area of composites research has emerged in the last two decades that utilizes nanoparticles fillers to alter the properties of polymers. Definitive results have not yet been achieved, but trends show that when processed properly, small amounts (< 5 wt%) of nanotubes can significantly increase the tensile and flexural modulus, tensile and flexural strength, inter laminar bonding, toughness and resistance to thermal degradation of FRPs.

The non-destructive techniques especially ultrasonic guided waves have been used widely for health monitoring of various kinds of specimens to detect the different type of damages that occur due to the presence of external forces (or usage) or manufacturing defects in the composites.

2.6 Gaps in the literature

With the introduction and application of nanotechnology, polymer nanocomposites have been showing promising results for the next generation material systems for structural applications. The gaps found in the literature are as follows:

1. Dispersion of carbon nanotubes in the polymer is an important factor and various techniques are present for their proper dispersion in the matrix. The dispersion techniques also have a significant effect on the properties of the resulting nanocomposites and not much research has been carried out in this field.
2. The effect of various modes of dispersion of CNT in epoxy has not been reported on the various mechanical properties.

3. Only limited work has been carried out to study the degradation behaviour of nanotube composites under hygrothermal loading conditions.
4. Limited works are available for damage detection & evaluation of in-service and manufacturing defects in carbon nanotube modified composites.

2.7 Objectives of thesis

From the identified gaps in the literature review, following objectives have been framed for performance evaluation of CNT modified fibre reinforced polymer composites.

1. To prepare and process functionalized multi-walled carbon nanotubes modified glass fibre reinforced polymer composites (GFRP) with a uniform and nanoscale dispersion of MWCNTs.
2. Investigate the behavior of fabricated MWCNT modified GFRP composites under tensile, flexural and hygrothermal loading conditions.
3. Develop a damage monitoring methodology for CNT modified GFRP laminates using ultrasonic guided waves that includes damages induced during manufacturing and usage.

The succeeding chapter outlines the research problem, objectives of the study and the methodology used to accomplish the goal.

Chapter 3. CNT modified GFRP composites

3.1 Introduction

This chapter presents the mechanical test result of fabricated GFRP composites in 0.0% CNT (neat epoxy), 0.1 wt% ACNT and 0.1 wt% PCNT compositions at stoichiometric ratio. In addition, to this the effect of modifying the stoichiometric ratio on the mechanical properties has also been looked into. Further, the relevant crosslinking reactions and morphological changes are studied and discussed in detail in this chapter. Besides this, the effect of choosing stirring over high-shear homogenizer for dispersion of carbon nanotubes in epoxy resin is also examined. Lastly, the effect of higher resin infusion temperature on the dispersion and mechanical behavior for both EP GFRP and ACNT GFRP compositions has also been explored.

3.2 Materials

Advantex[®] E-glass woven roving fibre mat (GF), WR310 purchased from Owens Corning Inc., (India) has been used as a primary reinforcement material. The supporting polymer matrix was DGEBA-based epoxy resin (AIRSTONE 780E) and poly(oxypropylene) diamine-based hardener (AIRSTONE 786H) with a stoichiometric weight ratio of 100:31 which was supplied by the DOW Chemical Company. For the purpose of developing polymer nanocomposites, pristine and functionalized CNTs were added. The commercially available non-functionalized multi-wall carbon nanotubes (MWCNTs) with a carbon purity of 99% and outer diameter of 10-20 nm and a length of 3-8 μm were purchased from Nanoshel (U.S.A.). While, the CVD synthesized MWCNTs functionalized with amino groups (<0.5%) (Nanocyl, NC3152) with a carbon purity of >95%, average length < 1 micron and diameters around 9.5 nm was purchased from Nanocyl S.A. (Sambreville, Belgium).

3.3 Methodology

3.3.1 CNT modified GFRP composites

Epoxy resin is defined as a molecule containing more than one epoxide groups. It is also termed as oxirane or ethoxyline group. The epoxy resin exists in several chemical structures, DGEBA being one of the widely used and is a short name for Diglycidyl Ether of Bisphenol-A

and its basic chemical structure is shown in Figure 3.1. DGEBA is synthesized by reacting bisphenol-A with epichlorohydrin in the presence of a catalyst.

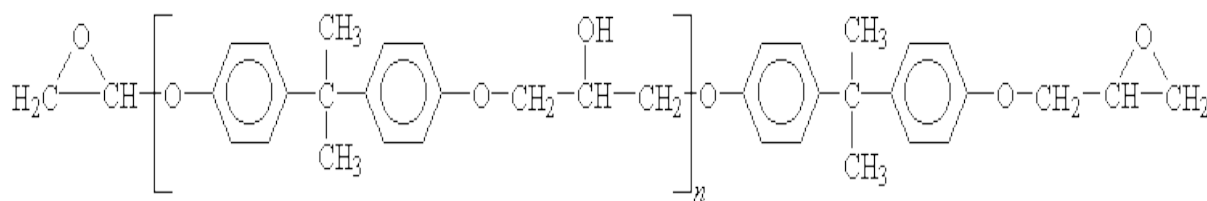


Figure 3.1: Chemical structure of DGEBA resin

It is essential for resin to undergo a chemical reaction into a hard, infusible and rigid material and it happens only after mixing it with the hardener. Among the wide variety of curing agents available for epoxy resins, the choice depends on the application, desired properties and the processing methodology. The amine hardener and epoxy resins undergo a nucleophilic ring-opening reaction as shown in Figure 3.2. Consequently, it transforms a low molecular weight resin into an infinite molar mass polymer, i.e. a 3-D cross linked network that consists of alternate segments of epoxy resin and amine hardener. Furthermore, the polymer chain length and density depends upon the number ‘n’ of epoxide chains in the matrix system.

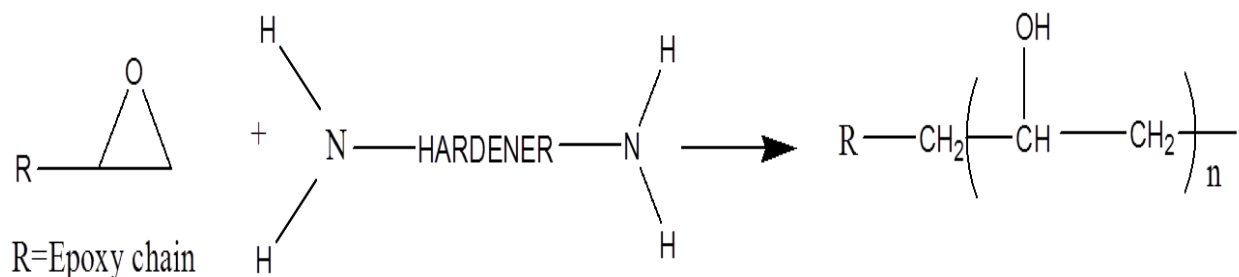


Figure 3.2: Reaction between epoxy resin and amine hardener

In addition, the curing agent concentration also significantly affects the curing mechanism and the resulting stiffness and strength properties of the cured material. From the above discussion, it seems that the hardener plays an important role in determining the cure kinetics. Where, different hardener types would reveal unique curing mechanisms, processing cycle (viscosity versus time) and gel-point. Further, it would eventually affect all properties of the cured composite [Cividanes *et al.* 2014]. Therefore, it is important to gather all the relevant information such as resin: hardener ratio, curing temperature and other matrix properties prior to its utilization. During the

present experimental work, the processing was carried out at stoichiometric ratio, unless specifically mentioned. On the other hand, addition of ACNT in epoxy resin during the processing stage, i.e. prior to the addition of amine hardener results in a pre-curing reaction as discussed ahead in section 3.4.1.1.

This chapter focuses primarily on the former i.e. mechanical properties, while the effect of curing mechanism has been discussed in detail in Chapter 7. In the present experimental study, CNT GFRP composites have been prepared by following the steps as detailed in the schematic diagram in Figure 3.3.

According to the 1st objective, the goal was to obtain uniform and homogeneous dispersion of both amino-functionalized and non-functionalized (pristine) nanotubes in an epoxy matrix as well as enhanced mechanical performance at low CNT content. In the present work, sonication and high-shear homogenization techniques based on its simplicity and effectiveness [Gojny *et al.*, 2003, Gojny *et al.*, 2004 (a, b), Shen *et al.*, 2007a] have been applied to account for uniform dispersion of nanotubes and to develop strong interfacial bonding between the matrix and nanotubes which, results in a cross-linked polymer chain. The formation of long and stable chain occurs due to the opening of the epoxide ring by nucleophilic attack of amino groups either from curing agent or functionalized nanotubes during its processing phase. The de-aerated epoxy: hardener mixture in stoichiometric ratio was infused to prepare thin laminates (containing 2 glass fibre plies) by using VARIM equipment.

However, a simplified procedure was adopted to prepare a mixture of epoxy resin and hardener as detailed in the next section.

3.3.1.1 Preparation of neat epoxy mixture

Pre-calculated amounts of resin and hardener were carefully weighed and placed in a beaker. AIRSTONE 786H, hardener was added to the resin and mixed using a mechanical stirrer at 500 rpm for about 5 min. As the curing reaction started, there was a gradual increase in the temperature of the mixture possibly due to the exothermic reaction [Rahaman and Mohanty 2014, Prolongo *et al.*, 2010].

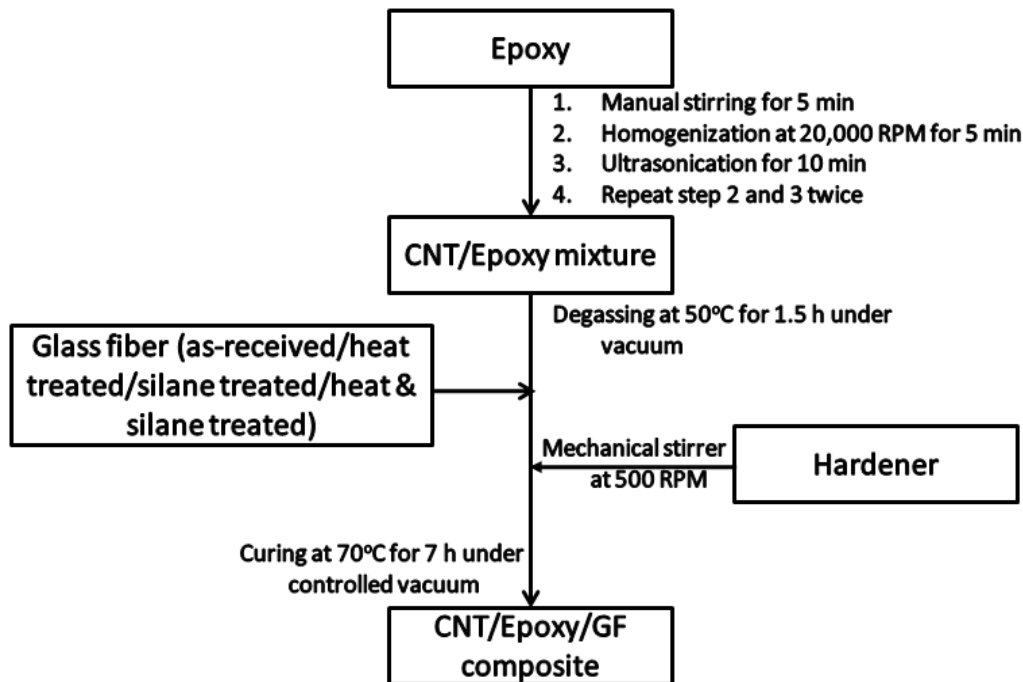


Figure 3.3: Schematic diagram of CNT GFRP composite preparation

3.3.1.2 Dispersion of CNT into epoxy resin

0.1 wt% of CNT was added to the epoxy resin and the mixture was manually stirred for 5 min. The procedure followed for preparing CNT/Epoxy homogeneous dispersion was same for both PCNT and ACNT. It was observed that the viscosity of the resin increased with addition of CNT during the stirring process. The CNT/Epoxy mixture was then subjected to high shear homogenization (T25), IKA Inc., at 20,000 rpm for 5 min. It was followed by ultrasonication using a sonicator probe (QSonica 700 with a power of 700W) at 40% amplitude for 10 min with a shutdown temperature set to 40°C. The beaker was submerged in ice-water to prevent the rise in temperature of the solution during the sonication process. The resulting CNT/Epoxy mixture was again subjected to high shear homogenization for 5 min and sonication for 10 min. The final CNT/Epoxy mixture was kept in a vacuum desiccator at 400 mBar for 1 h in order to remove the entrapped air bubbles in the mixture that might have been absorbed from the atmosphere during its processing phase. Finally, the stoichiometric ratio of hardener was added to the CNT/Epoxy mixture using a mechanical stirrer at 500 rpm for 5 min. An exothermic reaction occurred as soon as the hardener was added and to prevent the mixture from becoming too viscous, it was immediately infused into VARIM.

3.3.2 Fabrication of laminates using VARIM

Two glass fiber sheets with a cross-ply layup were used for the fabrication of fibre laminates in VARIM. Figure 3.4 illustrates the VARIM technique used in the manufacturing process of GFRP laminates.

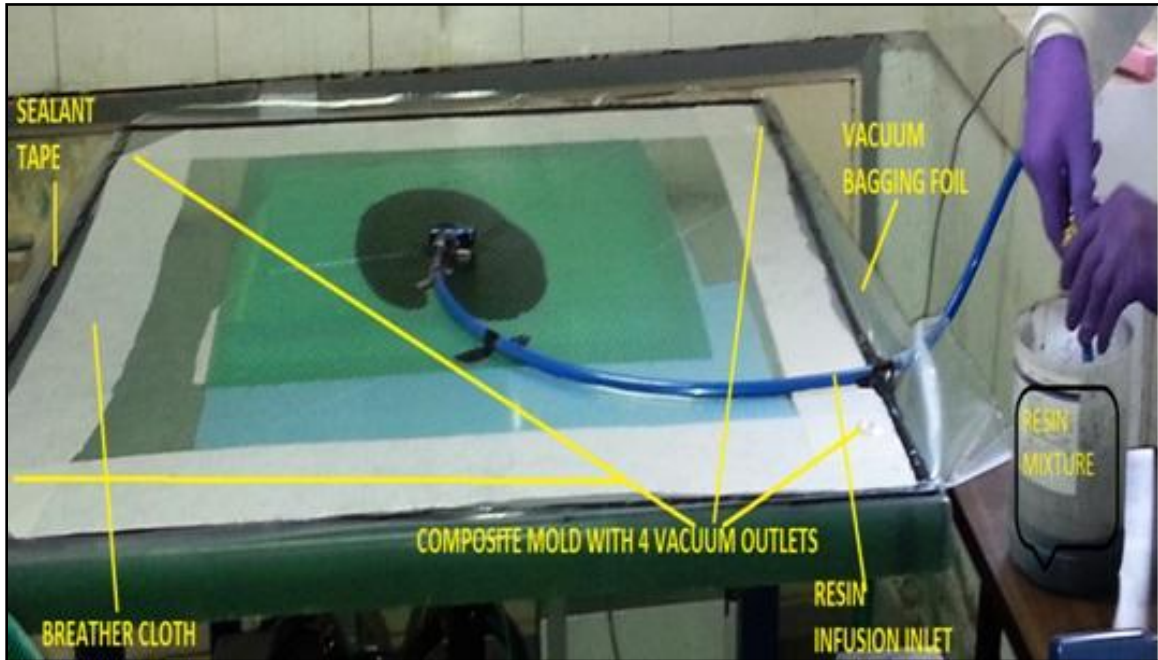


Figure 3.4: VARIM equipment for fabricating GFRP laminates

Firstly, the mold was set-up which was then followed by infusion of the mixture and lastly the recommended curing schedule was carried out. To begin with the fabrication process, woven roving glass fibres with a nominal weight of 300 g/m^2 were placed on the top of the composite mold. The glass fibre mat was followed by a layer of peel ply, perforated foil, a runner mesh, and breather cloth around the corners of the composite mold that covered the vacuum outlets. The sealant tape was pasted on the sides of the composite mold and the mold was covered with vacuum bagging film to enable achieving a huge vacuum in the mold. Additionally, a pipe was connected to a simple manifold at the center of the glass fibre mat so that the resin flow was equally distributed in all the directions in the composite mold. Subsequently, an outlet of the pipe was manually blocked using a stopper to prevent air from entering the mold. After the composite mold was ready and the vacuum of 1 mPa was attained, the final solution, i.e. either neat epoxy (as described in section 3.3.1.1) or modified epoxy with CNTs (as described in

section 3.3.1.2) was infused into the mold by placing the outlet of the pipe fully immersed in the beaker containing the mixture. The vacuum was maintained at 1–2 mPa throughout the experiment. After the matrix was successfully infused into the mold (as shown in Figure 3.4), the panel was cured at 70°C for 7 h thus, giving the composite an average thickness of 0.7 ± 0.1 mm.

For the experimental study, the composites were prepared with 74% fiber volume fraction using ACNT or PCNT nanotubes at 0.1 wt% concentration of the matrix. Figure 3.5 illustrates a schematic representation of the materials and equipments used for the preparation of GFRP composite laminates.

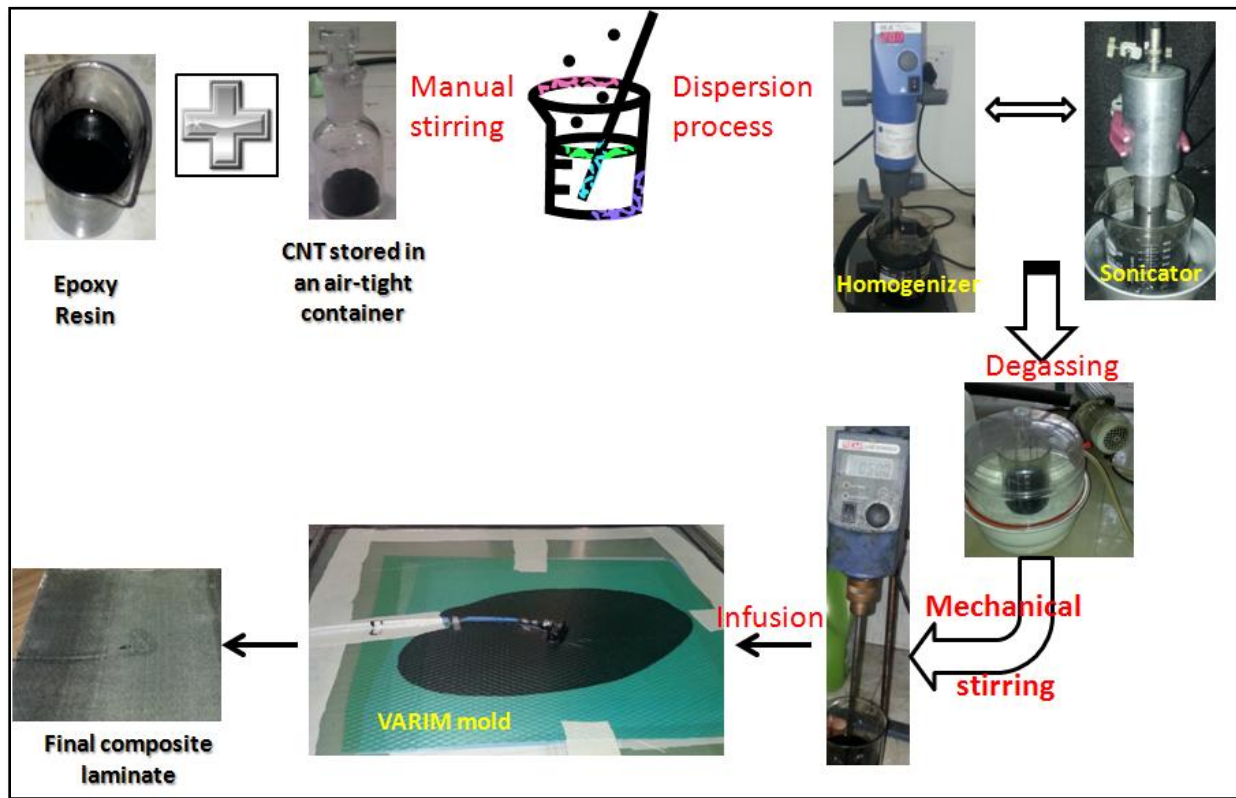


Figure 3.5: Schematic representation of the materials and equipments utilized in the preparation of GFRP composite laminates

3.3.3 Characterization

The pristine matrix and the composite characterization was performed before and after the curing process. The existence of bonding between the matrix constituents was verified by FTIR (Perkin-Elmer FTIR spectrometer) spectra. In order to prepare the samples, the liquid or

the powdered mixture was pressed into a pellet with KBr and scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

The fracture surfaces of the specimens tested under tensile and flexural loading conditions, were examined by SEM, JEOL (JSM 6510LV) at 20kV. Prior to the SEM analysis, all the specimens were sputter-coated with a thin layer of gold to avoid charging effects.

The morphology at the molecular level was investigated using TEM, Hitachi (H-7500) operating at 110 kV. The images showed the dispersion of CNTs in epoxy resin. One drop of the CNT/epoxy mixture was dispersed in ethanol and sonicated for 2 h. After sufficient sonication, a drop was placed onto the surface of a copper grid and excess solvent was removed by using a filter paper. The sample was then observed under TEM to identify the bonding of CNTs with the epoxy resin.

The tensile strength of the composites was determined using Zwick/Roell Z010 Universal testing machine at a crosshead speed of 2 mm/min. The specimens were prepared according to ASTM D3039 standard. System control and analysis were performed using TestXpert software supplied by Zwick/Roell. The GFRP specimens with a length of 250 mm and width of 25 mm were prepared using a marble cutter. An average of four samples was calculated and the same has been reported in this study.

Flexural tests were carried out according to ASTM D790 standard. The strength and modulus were evaluated using 3-point bending mode at a crosshead speed of 1.33 mm/min. For the flexural test, the span-to-width ratio was kept at 25.4 mm as per ASTM standards since the thickness of the specimens was less than 1.6 mm. The test specimen had a length of 60 mm, width of 12.7 mm and prepared using a marble cutter. Four samples were tested for each of the composite prepared and an average was taken, the same has been reported in the present study.

Short beam shear strength also known as Interlaminar shear strength (ILSS) has been calculated by following ASTM D2344 and using the formula shown in Equation (I):

$$ILSS = \frac{0.75 * F_{max}}{b * d} \quad (I)$$

The F_{max} values were obtained from the maximum breaking load during flexural testing. An average value of four samples was taken.

3.4 Results and Discussion

The goal of this chapter is to investigate various factors related to processing and fabrication of CNT GFRP composites. The reinforcement of EP GFRPs with CNTs would be successful if the hybrid composite satisfies two conditions, i.e. uniform and homogenous dispersion of nanotubes in the epoxy matrix, and an efficient, stress-transfer mechanism from the matrix to the nanotubes during external loading conditions. The study has been carried out by comparing the experimental results obtained with ACNT to that of PCNT nanotubes. In order to successfully accomplish this goal several different processing parameters have been experimentally investigated and the results obtained are discussed in following sub-sections.

3.4.1 Incorporation of nanotubes as reinforcement in EP GFRP composites

Since, this study was primarily based on the effect of ACNT reinforcement in EP GFRP composites, it was essential to observe their morphological behavior under the microscope. The ACNTs used in this study were supplied by Nanocyl, Belgium, had a high aspect ratio and high-specific-surface area. The microscopic (SEM) image of ACNTs at two different magnifications has been clearly shown in Figure 3.6. The entanglements seen in Figure 3.6 of ACNT are possibly due to strong forces of attraction between the carbon particles, which tend to achieve a metastable state. In order to overcome such agglomerates and achieve efficient dispersion of ACNT in an epoxy matrix, it was essential to choose the processing methods that incorporated stronger mechanical forces. As discussed earlier in Chapter 1, several processing techniques have reported uniform dispersion. But amongst those, the most effective and simple techniques are sonication and high-shear mixing and the same have been chosen in this study.

Therefore, sonication and high-shear homogenizing techniques have been combined to achieve homogenous dispersion of CNTs in epoxy resin and their step-by-step processing details are mentioned in Section 3.3.1.2. After obtaining a CNT/epoxy mixture, the first step was to quantify the chemical interactions of amino-CNTs with the epoxide groups of resin, followed by analyzing its dispersion under the microscope.

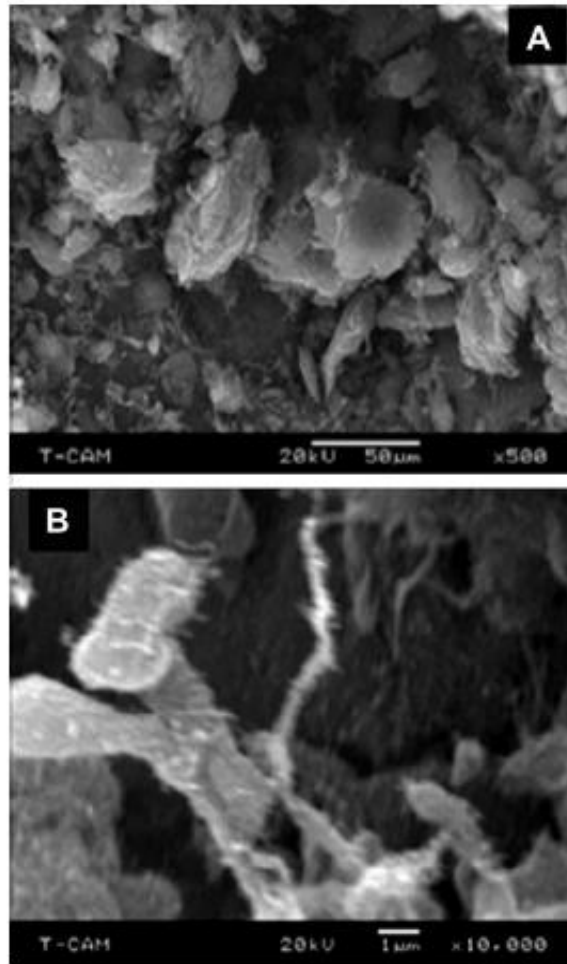


Figure 3.6: SEM picture of as-received MWCNT-NH₂ at magnification of 500x (A) and 1000x (B), [Source: Rahman *et al.*, (2012)]

3.4.1.1 Polymerization and TEM analysis

Quantitative analysis of the epoxy matrix, before and after curing, has been performed to determine the bonding between the matrix constituents by comparing their FTIR peaks. For this purpose, three different samples were analyzed by FTIR spectroscopy:

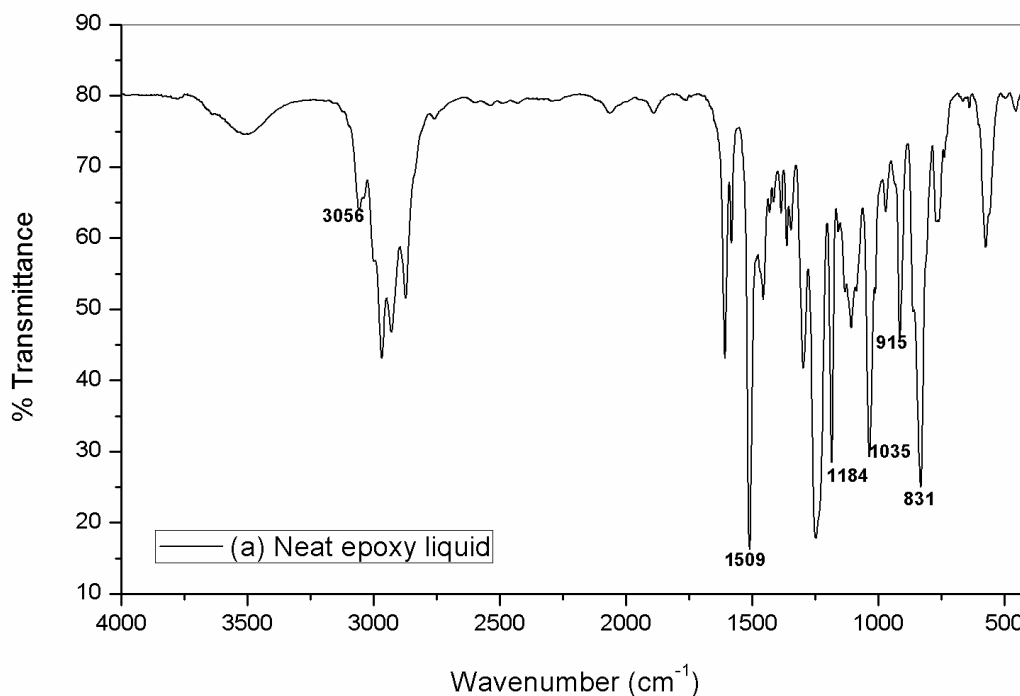
- (i) Neat epoxy (DGEBA resin) /0.0 wt% CNT (prior to its curing with hardener),
- (ii) EP GFRP composite and
- (iii) ACNT GFRP composite

Figure 3.7a illustrates the FTIR of DGEBA resin (EP in liquid form). The DGEBA resin contains bisphenol-A-(epichlorohydrin) epoxy with 1, 4-Bis (2,3 epoxypropoxy) butane and

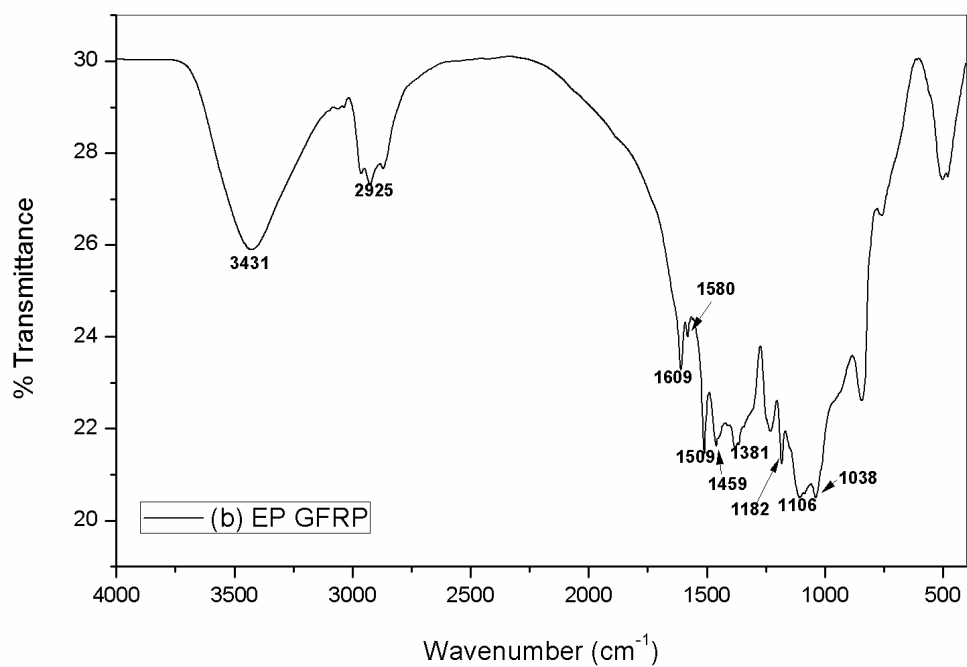
butanedioldiglycidyl ether groups. The peak of vital importance was seen at 915 cm^{-1} representing the C-O stretch vibrations in an oxirane ring. Another peak confirming the presence of epoxy resin was the symmetric stretch of the oxirane ring located at 3056 cm^{-1} . These two peaks were clearly visible in Figure 3.7a. The presence of ether group had been identified by the intense peak at 1035 cm^{-1} . Furthermore, stable aromatic rings, stretching were confirmed by the peaks at 831 , 1184 and 1509 cm^{-1} . However, after the curing reaction between the epoxy and amine hardener, shifts and elimination of the peaks were expected that verifies the occurrence of the cross linking reaction.

Figure 3.7b shows the FTIR spectrum of cross-linked AIRSTONE 780E with amine hardener in GF composite i.e. EP GFRP. The peak representing the oxirane ring (915 cm^{-1}) disappeared after the curing process. The phenomenon behind the disappearance of the peak from the spectrum is the ring-opening polymerization reaction (as shown in Figure 3.2). However, several new peaks were observed after the curing process. A broad peak appeared at 3431 cm^{-1} which is likely due to the secondary amine (N-H) and O-H stretching.

(a)



(b)



(c)

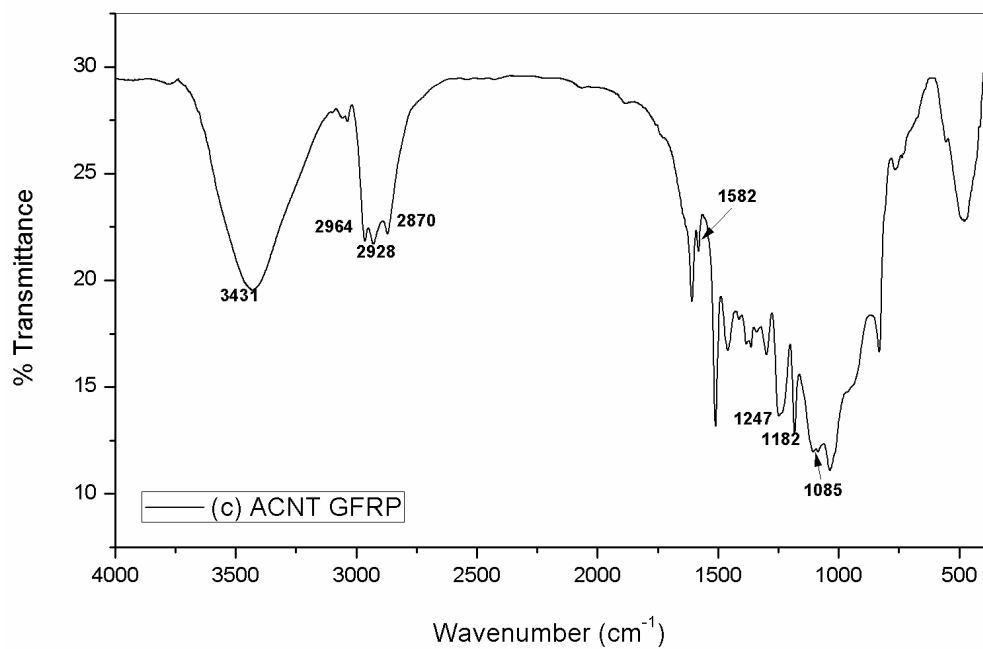


Figure 3.7: FTIR spectra of (a) Neat epoxy liquid sample, (b) EP GFRP composite, (c) ACNT GFRP composite

Interestingly, another strong peak observed at 2925 cm^{-1} is due to the $-\text{CH}_2-$ group stretching vibrations. Additionally, the strong band observed at 1609 cm^{-1} represents the stretching of $-\text{OH}$ group. Furthermore, the presence of several IR bands at 1602, 1580, 1509 cm^{-1} illustrates the stretching of aromatic rings. In addition, the appearance of bands at 1459 and 1381 cm^{-1} were possibly due to the bending of $-\text{CH}_2-$ and $-\text{CH}_3-$ groups. The stretching of $-\text{C}-\text{O}-\text{C}-$ could be seen by analyzing the peaks at 1251 and 1182 cm^{-1} . Furthermore, the peak at 1106 cm^{-1} characterizes the stretching of $-\text{C}-\text{N}$ group while the peak at 1038 cm^{-1} is due to the stretching of aliphatic ring ($-\text{C}-\text{O}-\text{C}-$). Therefore, the absence of transmittance of epoxide ring and presence of OH group and C-N group, as shown in Figure 3.8b validate the cross-linking polymerization process.

Figure 3.7c shows the FTIR spectra of ACNT GFRP composite with few similarities as seen in Figure 3.7b. Firstly, the epoxide group characteristic peak at 915 cm^{-1} was not present in the spectra, but, several other peaks emerged due to the addition of ACNT in the matrix. The single band at 3431 cm^{-1} showed the stretch of the primary amine group from the ACNT. The symmetric and asymmetric vibrations of ethylenediamine molecules have been identified by the peaks at 2964, 2928 and 2870 cm^{-1} . In addition, the presence of bands at 1581 and 1247 cm^{-1} , which corresponds to the N-H in plane and C-N stretching, respectively, were possibly due to the available amino groups on the surface of the CNT. The peak at 1182 cm^{-1} represents the stretching of amide group. Lastly, the small peak at 1085 cm^{-1} corresponds to the stretching of C-N of amine molecules. Therefore, the FTIR spectrum (Figure 3.7c) validates the coupling/curing reaction between DGEBA and ACNT. Furthermore, the verification of the stronger interfacial bonding between ACNT and the epoxy as borne out from the TEM images is discussed ahead.

Figure 3.8 demonstrates the morphology and cross-linking of amino-CNTs with epoxy resin as observed from a liquid ACNT/Epoxy sample. The sample was collected after ACNT was dispersed in epoxy resin, but prior to the addition of amine hardener in order to alleviate the effect of curing agent on the reaction mechanism.

From TEM image, it is observed that the majority of ACNTs are strongly bonded to the epoxy, likely through covalent linkages. Moreover, ACNTs (with approximately 9.5 nm diameter and length of <1 micron) were clearly visible in the TEM image (Figure 3.8) and in-fact individual nanotubes could be seen clearly.

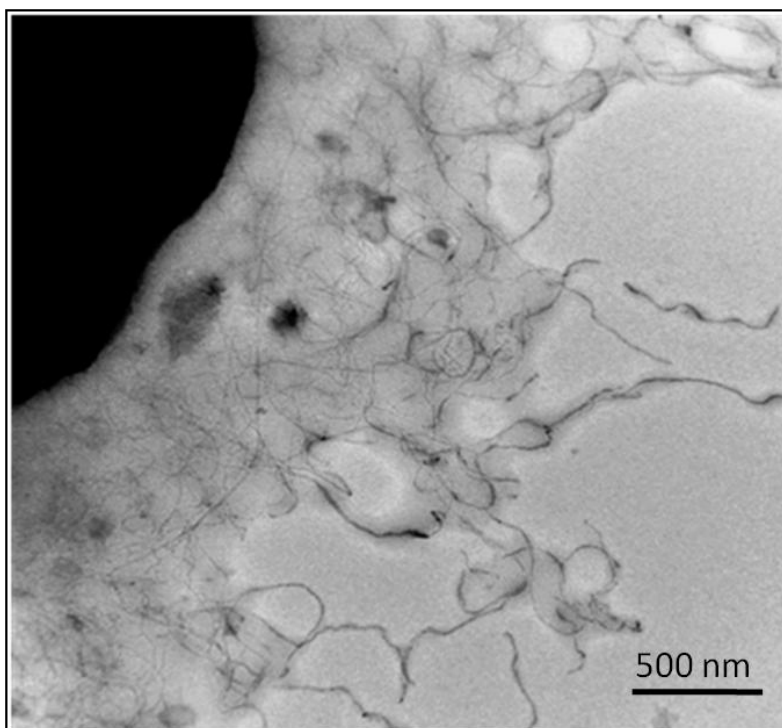


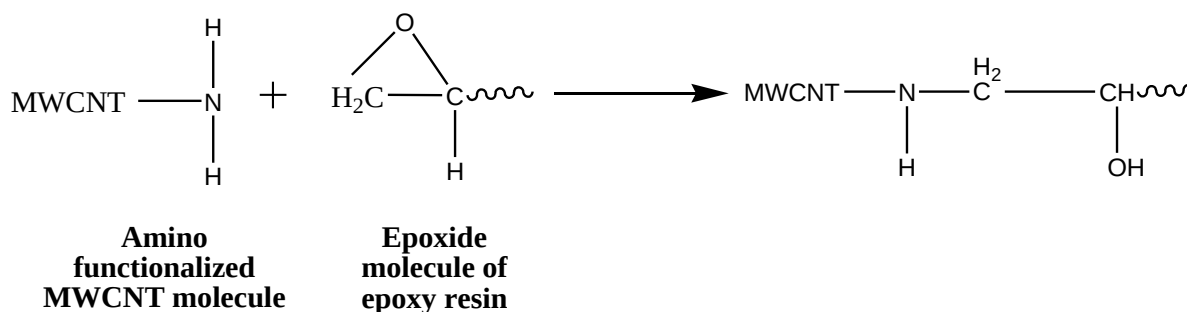
Figure 3.8: TEM image showing dispersion of 0.1wt% ACNT in epoxy resin

Thus, the image demonstrates the absence of CNT agglomerates which seems to be due to the presence of strong interfacial adhesion between amino-CNTs and epoxy matrix. Hence, FTIR peaks and TEM images were in correlation to support the stronger chemical interaction and occurrence of pre-curing reaction between the amino group of CNTs and the epoxide of resin i.e. before the addition of amine hardener. The polymerization/pre-curing reaction between amino groups of nanotubes and epoxide of resin follows a three step procedure as discussed ahead and illustrated in Figure 3.9.

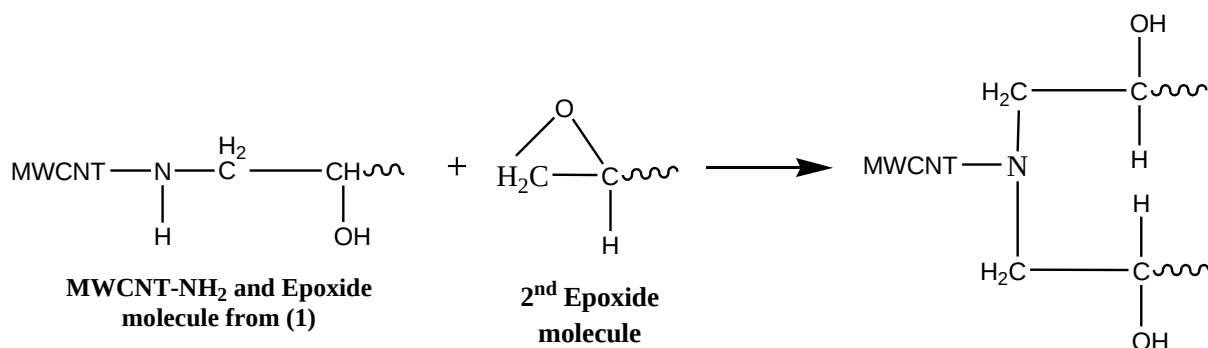
As described in Reaction 1 of Figure 3.9 after dispersing amino functionalized CNT in epoxy resin, a chemical reaction takes place between the amine group of CNTs and epoxide monomer groups that results in a nucleophilic ring-opening reaction and the formation of a polymer. The primary amine undergoes a reaction process to form secondary amines and continue to build long polymer chains. The product from reaction 1 further undergoes a chemical reaction with another epoxide molecule to form a polymer chain as shown in the mechanism of Reaction 2. Lastly, the resulting polymer chain further interacts with other epoxide groups present and starts building cross-linking polymer chain as shown in Figure 3.9. The presence of

primary and secondary amine groups has previously been observed in the FTIR spectrum (Figure 3.8c). This cross-linking reaction builds an interlocking mechanism in the resin which hinders the mobility of polymer chains in the system.

Reaction1: Reaction of ACNT with epoxide group of epoxy resin



Reaction 2: Reaction of product from Reaction 1 with another epoxide molecule of epoxy resin



Reaction 3: Cross-linking polymerization reaction between ACNT and epoxy molecules

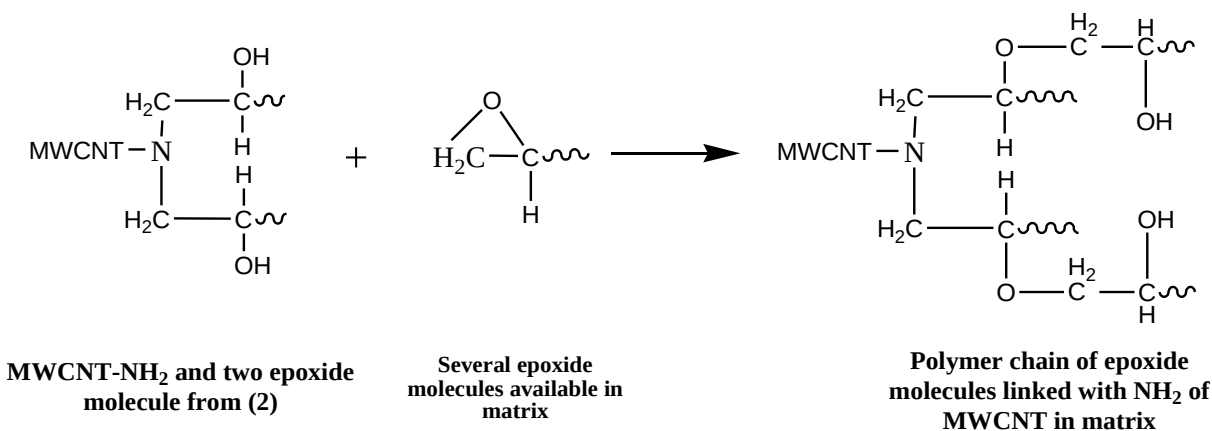


Figure 3.9: Mechanism of reactions between ACNT and epoxide group [Source: Hossain *et al.*, 2014]

Hence, due to this interconnected polymer chain and strong surface attractions, the interfacial bonding between ACNT and epoxy is significantly improved which further facilitates efficient load transfer from the matrix to CNTs. Such kind of interfacial bonding may result in improved mechanical properties [Gojny and Schulte 2004a, Gojny *et al.*, 2004b, Shen *et al.*, 2007a, Ma *et al.*, 2010, Rahman *et al.*, 2012, Salam *et al.*, 2013].

3.4.1.2 Mechanical behavior of CNT GFRP composites at stoichiometric ratio

The mechanical behavior of CNT GFRP composite depends on two main factors: the dispersion of CNTs in epoxy resin and interfacial bonding among the composite constituents which further depends upon the properties of the resin. However, in this study, a low viscosity epoxy resin was chosen as it assisted in improved dispersion of nanotubes, easy infusion and enhanced fibre wettability during VARIM manufacturing of nanocomposites. It is generally observed that after dispersing CNTs into polymer resin, it increases the resin viscosity and also the tendency to agglomerate. During the processing stage, it was seen that CNT/epoxy mixture became viscous and also took a little longer to infiltrate the fibre preforms as compared to a mixture with low viscosity. However, a low viscosity CNT/epoxy mixture could be obtained by two methods: (i) by increasing the temperature of the mixture beyond 40°C i.e. keeping the beaker in an electric oven, (ii) by using probe sonicator and high-shear homogenizer it generates strong ultrasonic waves and high shear rates. In this study, by adopting the second method the temperature of the CNT/epoxy mixture was recorded at about 60°C. Consequently, it made the dispersion of CNT in the epoxy resin more efficient and also built strong covalent bonds. Hence, it can be stated that such factors affect the fibre-matrix interface adhesion as well as mechanical properties of the composite material.

Figure 3.10 shows the tensile and flexural strength of the laminates versus the type of CNT in the matrix. The EP GFRP sample data has been taken as a reference in order to compare the mechanical behavior of the CNT reinforced GFRP composites.

From the figure it can be interpreted that the tensile strength increased by 42% on addition of PCNT while it decreased by 15% for ACNT composites. Similar results for improved tensile properties in epoxy matrix incorporated with PCNTs were also reported by other researchers [Thostenson and Chou 2006, Mallick 2007, Diez-Pascual *et al.*, 2011]. Such

behavior can be credited to the uniform dispersion of PCNT in resin, which facilitated load transfer from the matrix to CNTs, thus enhancing the longitudinal strength of the composite material. Additionally, a few more reasons that possibly support higher properties for PCNT are: (i) during our experiments, it was observed that the viscosity of the CNT/Epoxy mixture was not affected by adding pristine nanotubes as compared to amino-CNTs. This possibly assisted in the better wettability of glass fibres, reduced voids and strong fibre-matrix interface. Secondly, it is possible that the stress was completely transferred from the weak matrix to the uniformly dispersed pristine nanotubes in epoxy resin. Lastly, the matrix protected the individual fibre strands from breaking and/or pullout as evident from SEM images (refer to Figure 3.11a). In addition, SEM image depicts more matrix cracking than fibre breakage in PCNT GFRP samples which was missing in ACNT GFRP samples (Figure 3.11b).

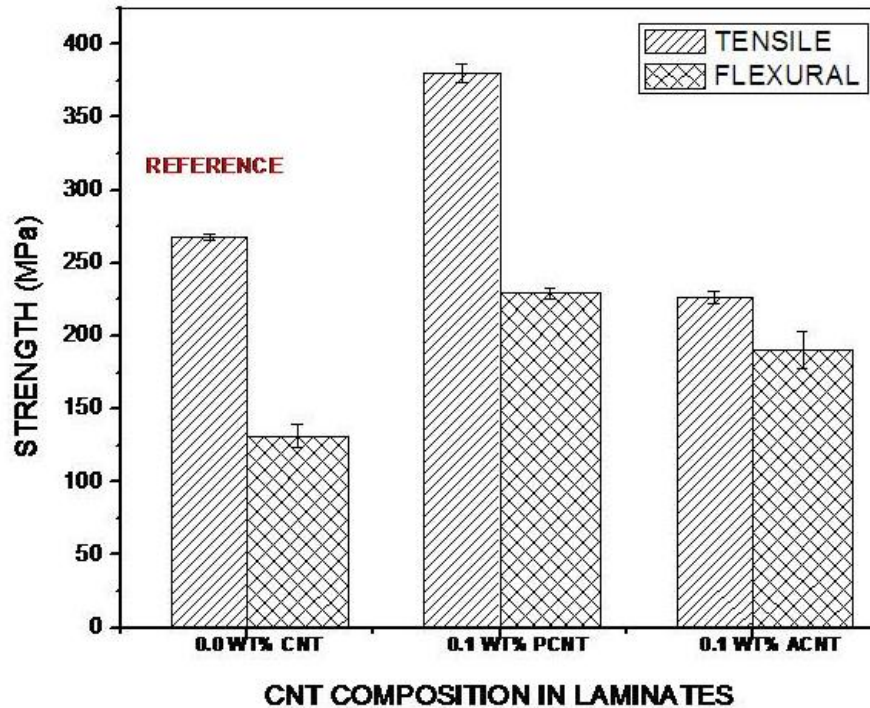
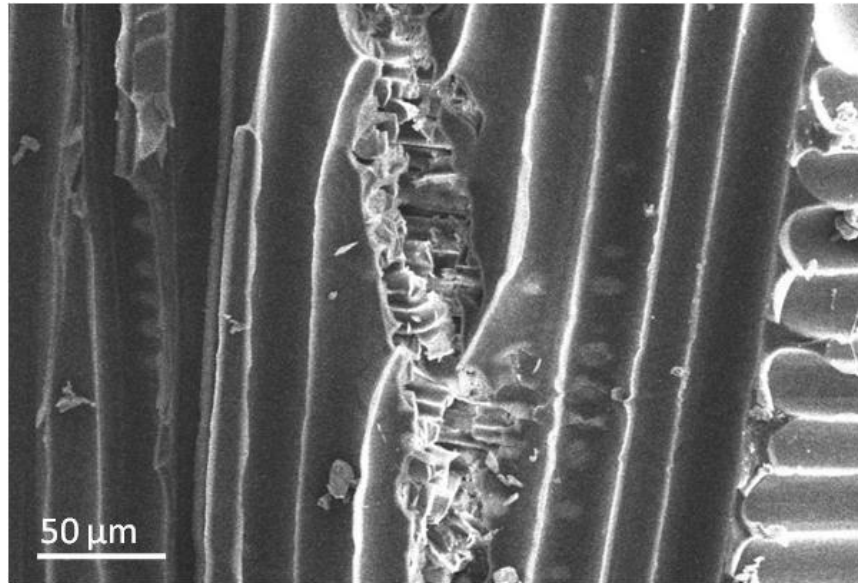


Figure 3.10: Effect of CNT composition on the tensile and flexural strength

Further, a slight decrease in the tensile strength of ACNT GFRP composite is possibly due to the stiffening effect caused by the strong covalent bond between the amino groups on the surface of CNT and the matrix. A study by Ci and Bai [Ci and Bai 2006] reported that if the matrix is too rigid there is negligible effect on the mechanical properties by the addition of CNT

in the base epoxy matrix. The epoxy matrix used in the present experimental study has a tensile modulus of approximately 3.3 GPa, which is significantly greater than 2.4 GPa reported in the study by Ci and Bai. Since the matrix chosen is more rigid, a decrease in tensile properties was expected. The soft and ductile matrix allows stronger interfacial interaction, whereas the reverse is true for rigid matrix.

(a)



(b)

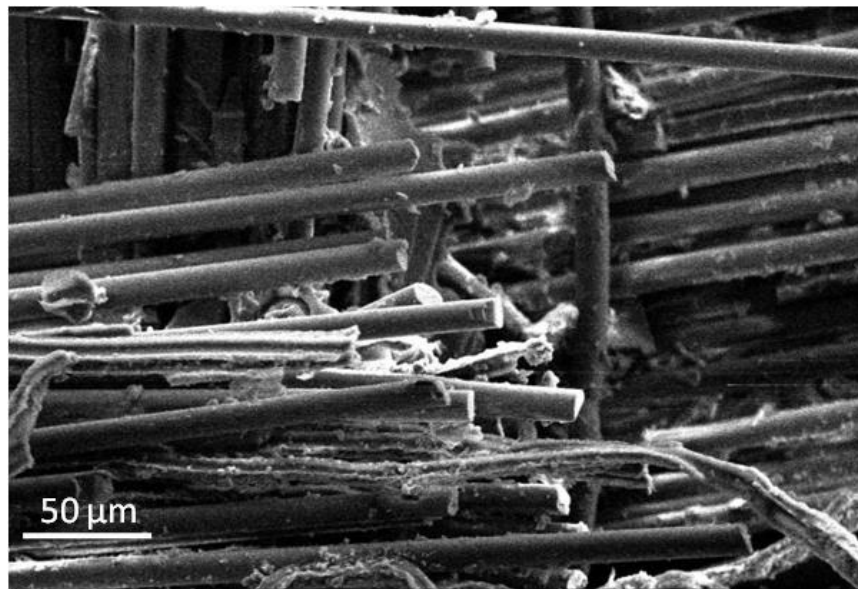


Figure 3.11: SEM image of fractured surface of tensile specimens of: (a) PCNT GFRP and (b) ACNT GFRP composites

On the other hand, the flexural strength of composites showed an improvement of 74% and 46% in PCNT GFRP and ACNT GFRP composites respectively, as compared to the control sample. The significant increase in flexural strength of ACNT GFRP composites is possibly due to the transfer of stress from the surrounding matrix to the glass fibres. The fibres being stronger than the matrix do not allow fibre breakage instead, get pulled out from the matrix. Since, the fibres had larger dimension in the longitudinal direction it resulted in enhanced ductility and strength as compared to the EP GFRP sample.

A similar behavior was also observed for tensile and flexural modulus of CNT GFRP composites as shown in Figure 3.12. In the case of PCNT GFRP composites an increase of 26% and 50% was seen for tensile and flexural modulus, respectively as compared to reference sample. Whereas, for ACNT GFRP composite the flexural modulus increased by 36%, but the tensile modulus again showed a drop of 15%.

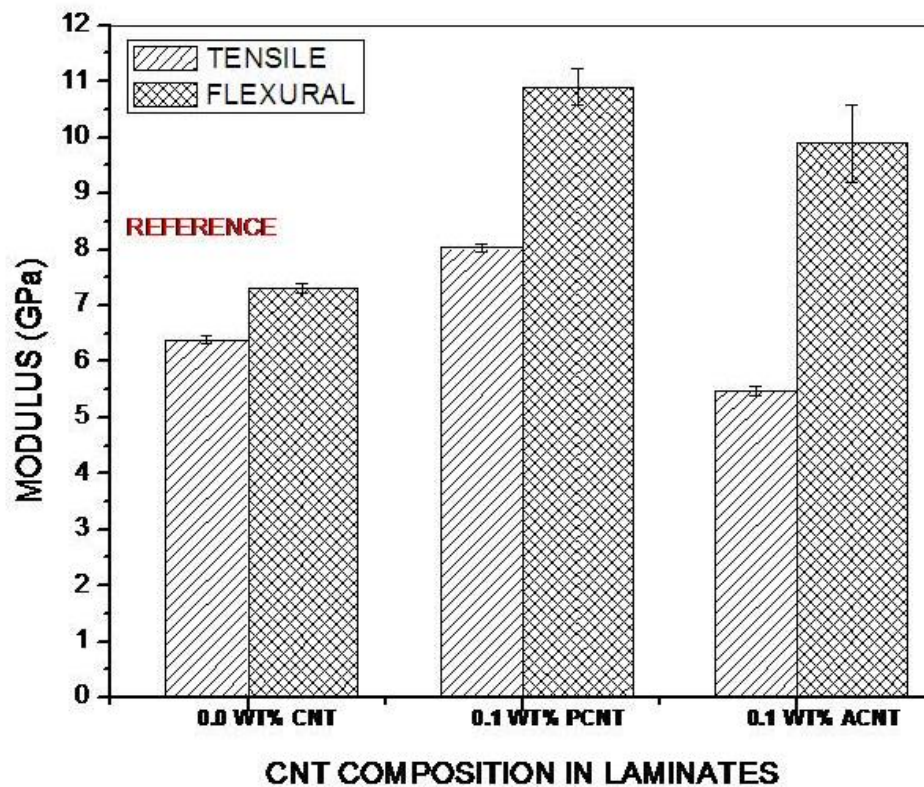


Figure 3.12: Effect of CNT composition on the tensile and flexural modulus

To improve the elastic modulus by incorporating CNTs in the composite has been a challenging task and also explored by various researchers [Bekyarova *et al.*, 2007a, Gojny *et al.*, 2005b, Iwahori *et al.*, 2005, Quaresimin and Varley 2008, Godara *et al.*, 2009]. In general, the experimental results demonstrate significant improvement in the flexural strength (Figure 3.10) and modulus (Figure 3.12) by incorporating nanotubes in the EP GFRP composites, [Iwahori *et al.*, 2005, Sanchez *et al.*, 2013]. Apparently, the enhancement in flexural properties is due to the fibre breakage followed by small increments in strength, possibly due to the matrix cracking and local delamination occurring inside the sample.

To further validate the above findings, stress-strain curves under both tensile and flexural loading conditions were plotted for the three samples as shown in Figures 3.13 and 3.14.

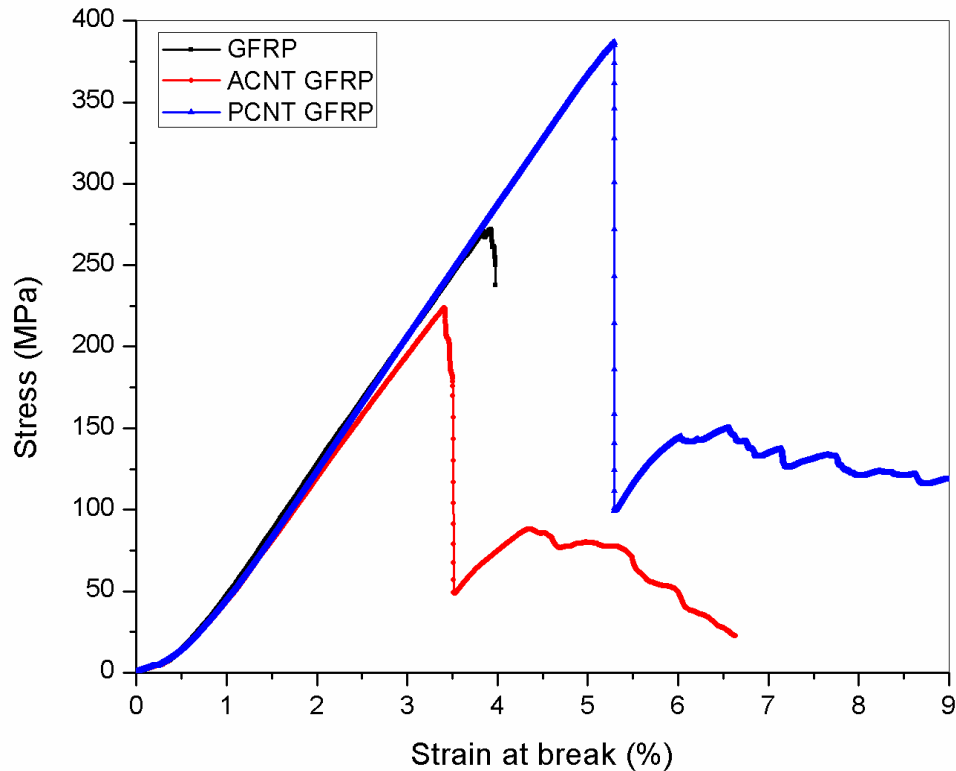


Figure 3.13: Stress-strain behavior with the addition of nanotubes in EP GFRP composites: Tensile loading

From Figure 3.13, it can be stated that incorporating CNTs did not have much effect on the tensile modulus of EP GFRP composites at low strain levels. Such behavior can be attributed to the fact that the stiffness of GF dominates the elasticity of EP GFRP samples, being stiffer as

compared to the epoxy matrix. However, at higher strain levels, CNT GFRP composites are stiffer than the neat epoxy ones. The increase of stiffness is associated with an increase in strain due to fibre straightening during the tensile tests [Genedy *et al.* 2015, Chou 2005]. On the other hand, as strain level increases, damage accumulates inside the matrix which initiates fibre debonding from the composite interface. As a result, stiffness decreases and eventually causes failure of the material. The findings from the stress-strain graphs also illustrate the similar trend as observed in Figures 3.10 and 3.12 i.e. PCNT GFRP samples have much higher stiffness and strength vis-à-vis ACNT GFRP and EP GFRP samples.

Few other observations made from Figure 3.13 are: (i) stress increases linearly as a function of applied strain for all composite matrices up to a certain limit, after which a sharp fall is observed, approximately in the range of 3.5-4.5%, (ii) ACNT GFRP composites demonstrated slightly more ductile behavior as compared to EP GFRP specimens. This is due to the strong fibres which tend to resist fibre breakage but, got pulled out after sustaining the external load along its length. Whereas, PCNT GFRP composites showed the maximum strain value, 5.4%, and significant ductile behavior as compared to brittle failure for EP GFRP composition. The stress-strain behavior observed in Figure 3.14 under flexural loading conditions also shows similar results. The significantly enhanced ductile response for PCNT GFRP composites is likely due to slower crack propagation through the fibres, followed by an increase in strength due to matrix cracking and local delamination occurring in the specimen. Also, the matrix strongly adhered to the glass fibres and protected the occurrence of fibre delamination on the application of external load as discussed earlier and evident from Figure. 3.11a. On the other hand, ACNT GFRP samples have demonstrated better flexural response than tensile as compared to EP GFRP sample. It is believed that there is a complex mechanism behind such performance and an attempt has been made to explore the same. Although it is observed that amino-CNTs improve the dispersion in epoxy resin but, at the same time it increases the viscosity of the resin mixture and also affects the degree of cure of epoxy resin at the time of infusion, which was missing for PCNT samples. As stated earlier, the higher surface area of amino-CNTs results in a higher viscosity of ACNT/Epoxy mixture during the processing stage, which made the fibre wetting difficult and possibly led to the formation of voids in between the fibre layers. These voids during early stages of loading become a source of crack initiation and are followed by fibre delamination and breakage. SEM images of fractured tensile specimens of ACNT GFRP sample

(as shown in Figure 3.11b) also clearly reveal fibre pull-out and matrix cracking along the fibre surface.

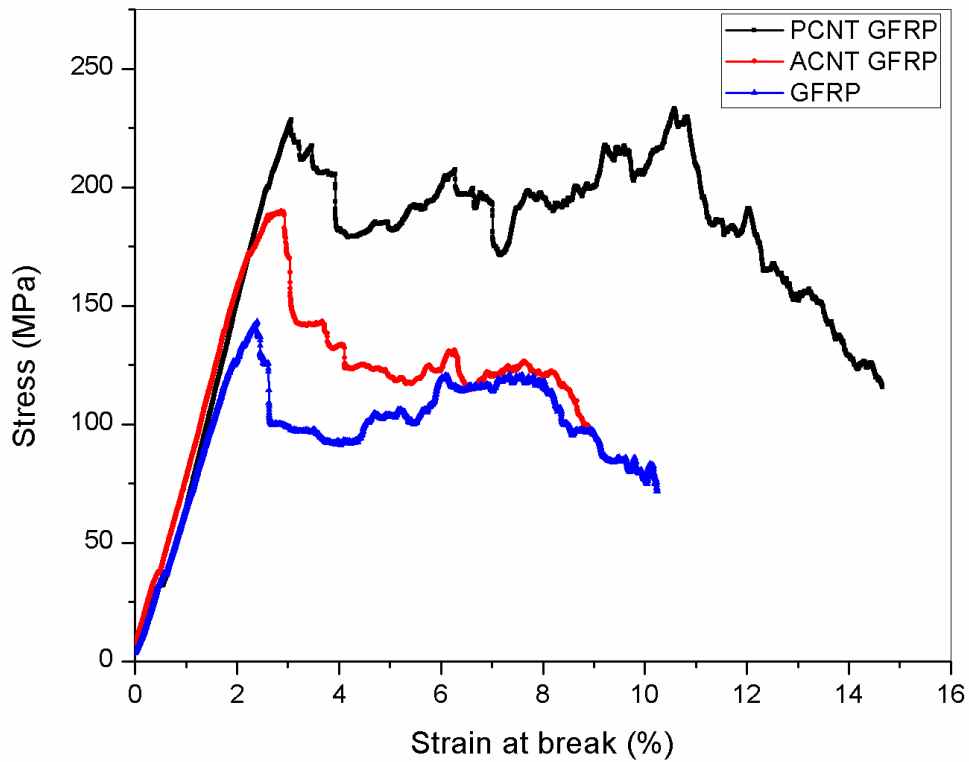


Figure 3.14: Stress-strain behavior with the addition of nanotubes in EP GFRP composites: Flexural loading

In addition to the above stated reasons, it is well known that during the functionalization process of nanotubes they are oxidized in high concentration acids, which often introduce damages on the surface of the CNT, reduce its aspect ratio and decrease the interfacial area for bonding [Monthieux *et al.*, 2001, Shen *et al.*, 2004]. Hence, the presence of occasional voids, lower surface area and inability to completely transfer external stress from the matrix to the nanotubes possibly caused degradation of the mechanical properties. Interestingly, the results obtained for ACNT composites with stoichiometric ratio are in agreement with those stated by Gude [Gude *et al.*, 2012]. The literature supports the above mechanical response for ACNT GFRP composites by stating that in a highly cross-linked network the addition of amino-CNTs shows a detrimental effect on the curing since its addition, delays the peak of reaction and/or prevents the resin to obtain their optimal properties [Bae *et al.*, 2002, Lopez *et al.*, 2009, Rico *et*

al., 2011]. But, it is important to point out that EP GFRP composites prepared using functionalized CNTs especially, amino-CNTs, are considered to be more efficient reinforcing agents, usually when incorporated at higher loading levels i.e. >0.1 wt% [Sanchez *et al.*, 2013].

Overall, the reinforcement of epoxy resin with nanotubes was found to increase the flexural modulus and strength irrespective of the functional group, since those are fibre-dominated properties. Thus, from the experimental findings, it can be concluded that PCNT are better reinforcing fillers than ACNT in epoxy resin at the stoichiometric ratio when considering the mechanical properties.

3.4.1.3 Effect of resin: hardener ratio

In the previous section, for the composites prepared using stoichiometric ratio (i.e. 76% resin), all the amine hydrogen reacted with the epoxide groups, thus giving a network of interconnected rings. These rings contain two or more epoxide chains after reacting with the active amine functional group. However, if the matrix contains an excess of epoxy groups, then all the primary and secondary amines will react with 80% of the epoxy groups of DGEBA resin. The left 20% epoxy molecules will be freely available in the matrix, thus improving its flexibility but, lowering other mechanical properties at the same time. While in the case of matrix with excess amine, all the epoxy groups react with primary amines while leaving a few secondary amines unreacted. According to Morgan [Morgan *et al.*, 1984], epoxy tends to give branched structures, and possibly results in rings with partially reacted triamine molecules and epoxide chain. Another study by Gude [Gude *et al.*, 2012] reported that, changing the stoichiometric ratio of the resin in the matrix has a greater effect on the properties of the resin as compared to modifying the matrix with the addition of CNTs. It was also stated that CNTs showed better dispersion in the amine excess matrix because at the nanoscale, the hardener molecules tend to adsorb into the inner layer of ACNT during the curing process and result in improved mechanical performance. Considering the above mentioned facts, it became interesting to explore the dispersion and mechanical behavior of CNT modified composites for a non-stoichiometric composition. Hence, the amine content was increased by 25% in the matrix and is referred to as 69% for discussion in this section.

Table 3.1 summarizes the mechanical properties of composites prepared in amine-rich resin system as compared to those obtained from stoichiometric system. Overall, the results in Table 3.1 highlight enhancement in mechanical properties by increasing the amine content in the resin, particularly for composites prepared with amino-CNTs. Similar behavior has also been observed by other researchers globally [Palmease and McCullough 1992, Meyer *et al.*, 1995, Fernandez-Nogroa *et al.*, 1996, Calventus *et al.*, 2001, Prolongo *et al.*, 2010, Gude *et al.*, 2012].

Table 3.1: Summary of mechanical properties obtained by modifying epoxy: hardener ratio for different GFRP compositions

S.No.	Specimen	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Interlaminar Shear Strength (MPa)
1a	EP GFRP (76% resin)	6.4	268	7.3	131	1.8
1b	EP GFRP (69% resin)	5.8	306	13.0	233	2.9
2a	PCNT GFRP (76% resin)	8.0	380	10.9	229	3.0
2b	PCNT GFRP (69% resin)	6.7	248	11.0	224	3.1
3a	ACNT GFRP (76% resin)	5.7	227	9.9	191	2.5
3b	ACNTGFRP (69% resin)	8.9	369	10.4	255	3.5

For EP GFRP composites (rows 1a and 1b in Table 3.1), the Young's modulus of 6.4 GPa was found to be higher for 76% composition and dropped by approximately 10% on increasing the amine concentration in the matrix. However, other mechanical properties increased significantly for 69% composition, such as flexural strength (+ 77%), flexural modulus (+ 79%), and tensile strength (+ 14%). The increase in strength, especially during bending conditions demonstrates the presence of a strong fibre-matrix interface. In addition to this the stiffness also improved possibly due to strong cross-linked polymer network chain while,

contradicting the results reported in literature wherein, a decrease in flexural modulus is reported for amine-rich resin system [Palmese and McCullough 1992, Meyer *et al.*, 1995, Fernandez-Nogroa *et al.*, 1996, Gude *et al.*, 2012]. Moreover, samples with 69% composition showed an enhanced ductile behavior as compared to 76% composition samples which exhibited brittle failure. It was possibly due to the fact that, free uncured molecules were available in the composite which tend to further increase the ductility of the laminates. Thus, the experimental findings suggest that excess amine content has a positive effect on flexural modulus, flexural and tensile strength. Therefore, it was important to investigate if similar trend was also apparent by reinforcing epoxy matrix with nanotubes in an amine-rich resin composition.

Interestingly, ACNT GFRP composites (at 69% matrix composition, refer to row 3b in Table 3.1) also showed remarkable improvement in the mechanical properties. The maximum enhancement in tensile and flexural properties among all the samples was observed for ACNT GFRP (69% resin) samples (row 3b in Table 3.1) i.e. an increase in tensile modulus by 39%, tensile strength by ~ 38%, flexural modulus by ~ 43%, flexural strength by 95% and ILSS by 94% as compared to the EP GFRP sample prepared with a stoichiometric ratio (refer to row 1a in Table 3.1). However, comparing with ACNT GFRP (76% resin) composition (row 3a in Table 3.1), there was an improvement by 62% in tensile modulus, 63% in tensile strength, ~5% in flexural modulus, 33% in flexural strength and 40% in ILSS. Furthermore, PCNT GFRP (69% resin) composites, demonstrated an improvement of 5% in tensile modulus, 52% in flexural modulus, 71% in flexural strength and 69% in ILSS strength (row 2b in Table 4.1) vis-à-vis EP GFRP sample (row 1a in Table 3.1). Although, ACNT GFRP samples (at stoichiometric ratio) showed improvement in flexural strength, but it was slightly lower than that of PCNT GFRP samples.

Further improvement in flexural strength can be obtained by increasing the loading level of amino-CNTs in resin and supportive reasoning has been discussed earlier. Therefore, considering flexural strength for ACNT GFRP composition it is possible that on increasing its concentration in the matrix, it would show a better reinforcing effect on the material properties, thus suggesting stronger interfacial bonding and presence of robust covalent bonds. As a result, their performance would certainly overpass that of PCNT GFRP composites for all resin compositions.

Another noteworthy finding from this experimental study is that Young's modulus and tensile strength of ACNT GFRP samples have scored over PCNT GFRP samples in an amine-rich resin composition as evident from rows 2b and 3b in Table 3.1. This is due to the strong covalent bonding between the epoxy resin and amino groups of CNT developed during the processing phase. Also, after infusion into the glass fibres, the matrix strongly held onto the fibre surface and prevented crack initiation inside the fibre-matrix interface. The presence of excess amine molecules in the epoxy matrix minimized the increase in the viscosity of the CNT/Epoxy mixture, improved fibre wettability and built stronger interconnected network inside the composite. As a result, the interface was enhanced considerably, which is evident from the increase in strength and ILSS properties.

However, these results (for 69% epoxy composition) contradict with those reported by Gude [Gude *et al.*, 2012], which mentioned that the reinforcement effect of CNT was almost negligible in amine-rich resin composition. These results showed an improvement in flexural modulus in amine-rich composition over stoichiometric (76% composition) but not comparable to resin-rich system. However, the results reported here are different from their study possibly due to the use of different curing agent. It is believed that the curing mechanism gets affected as it depends on the type of resin and hardener used, which subsequently affects the mechanical performance of the composites. Another reason to support such behavior is that, the excess amine groups in the matrix underwent nucleophilic ring-opening mechanism with the free available epoxide groups and formed a strong interconnected network which was efficient in transferring the load from the matrix to CNTs under stress.

To further validate the above mentioned results, stress-strain graphs for CNT GFRP samples at 69% and 76% compositions have been shown in Figure 3.15. It is evident from the figure that there was an effective stress-strain mechanism between amino-CNTs, epoxy resin and glass fibre for amine-rich resin systems. The stress-strain graph for ACNT GFRP (69% composition) is almost overlapping with PCNT GFRP (76% composition) except that there was a sudden failure of the specimen. On the other hand, for PCNT GFRP samples prepared in amine-rich resin matrix, the strain bearing capacity reduced drastically as the material showed brittle failure as compared to the ductile behavior observed for stoichiometric ratio samples. This suggests that there was poor fibre-matrix interfacial bonding and the stress was primarily

concentrated on the matrix. As a result, during tensile loading conditions the glass fibres started to debond along with matrix cracking and thus failed abruptly. These results seem to be in correlation with the other mechanical properties studied for PCNT GFRP samples.

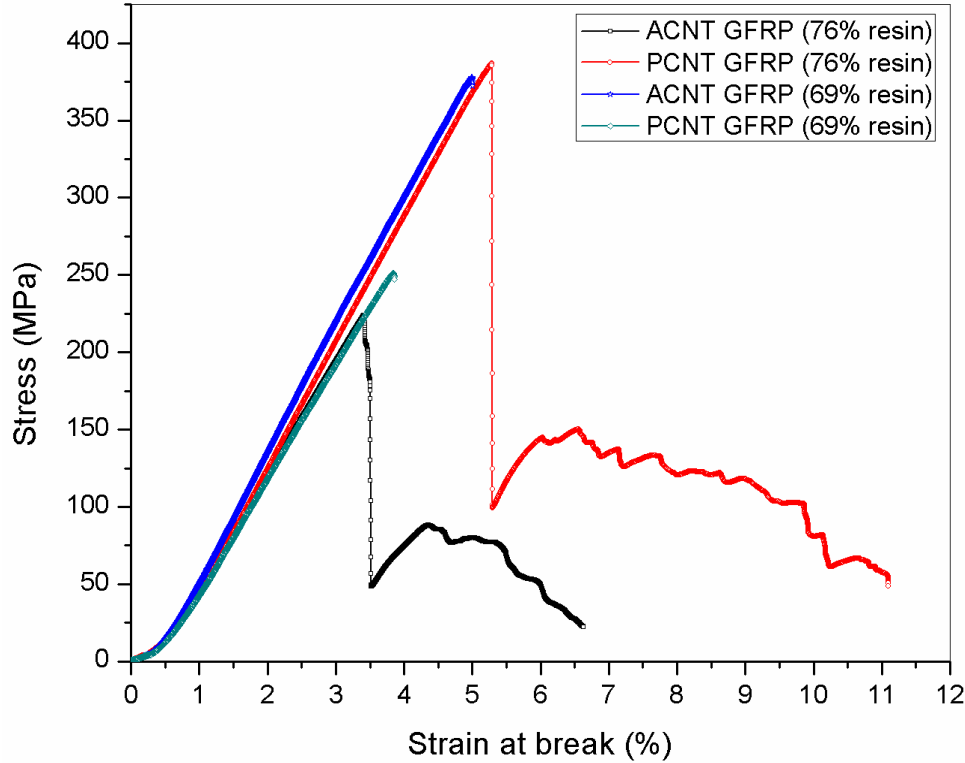


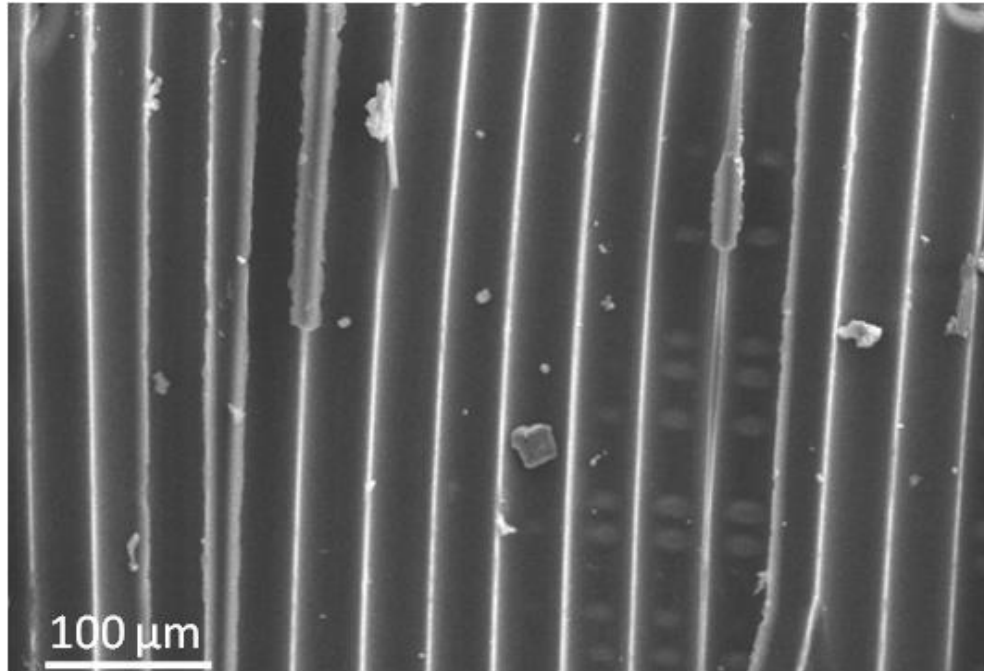
Figure 3.15: Stress-strain behavior for ACNT GFRP and PCNT GFRP composites in amine-rich resin matrix: Tensile loading

Subsequently, examination of the fractured surfaces of the material under microscope assisted the relating mechanical behavior with failure mechanisms as discussed earlier. In general, SEM images support the quantitative results obtained through mechanical tests of the various composites discussed above. Figures 3.16 (a) – (e) shows the SEM images of the fractured control sample (EP GFRP) and hybrid GFRP samples prepared with different epoxy: amine ratio.

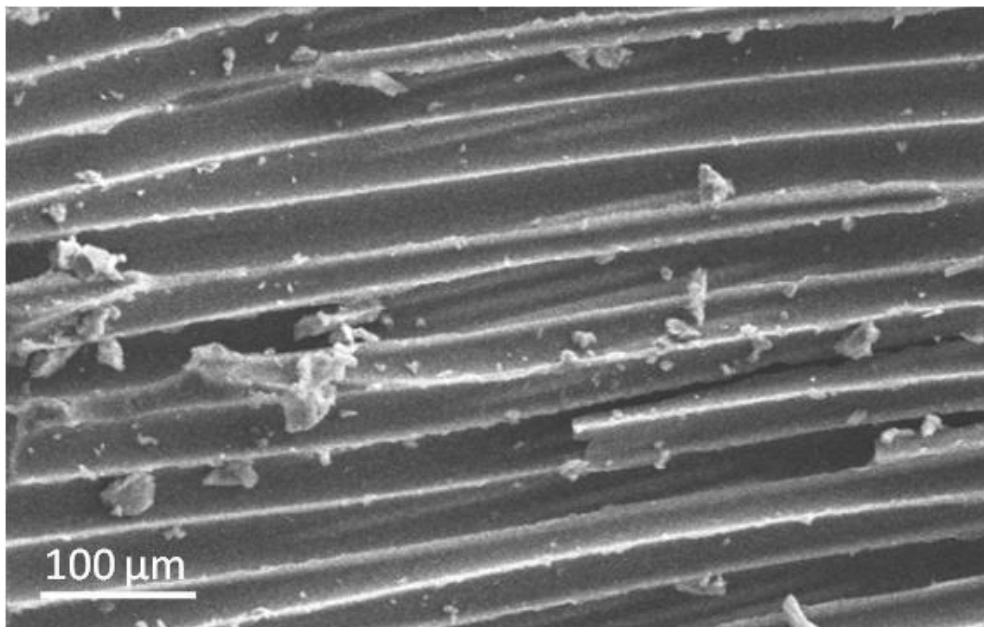
The fractured surfaces revealed rougher surface for all the samples that incorporated CNTs as compared to the clean and smooth surface observed in the EP GFRP sample (Figure 3.16a). ACNT GFRP composites illustrate better fibre-matrix interface adhesion visualized by fewer number and smaller sized matrix particles over the fibre surface (refer to Figure 3.16b).

The image has confirmed the successful dispersion of ACNT in the epoxy matrix and highlights the stability of the dispersed amino-CNT in the matrix even after the curing process. Similar results with respect to ACNTs illustrating better bonding for longer time durations have also been reported by other researchers [Ma *et al.*, 2010].

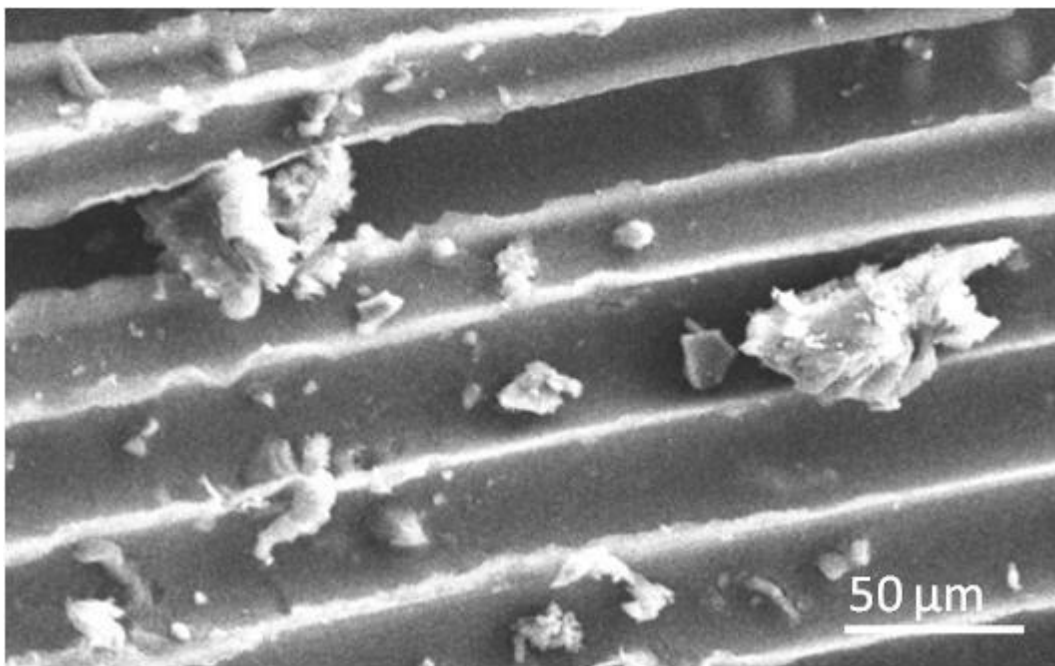
(a)



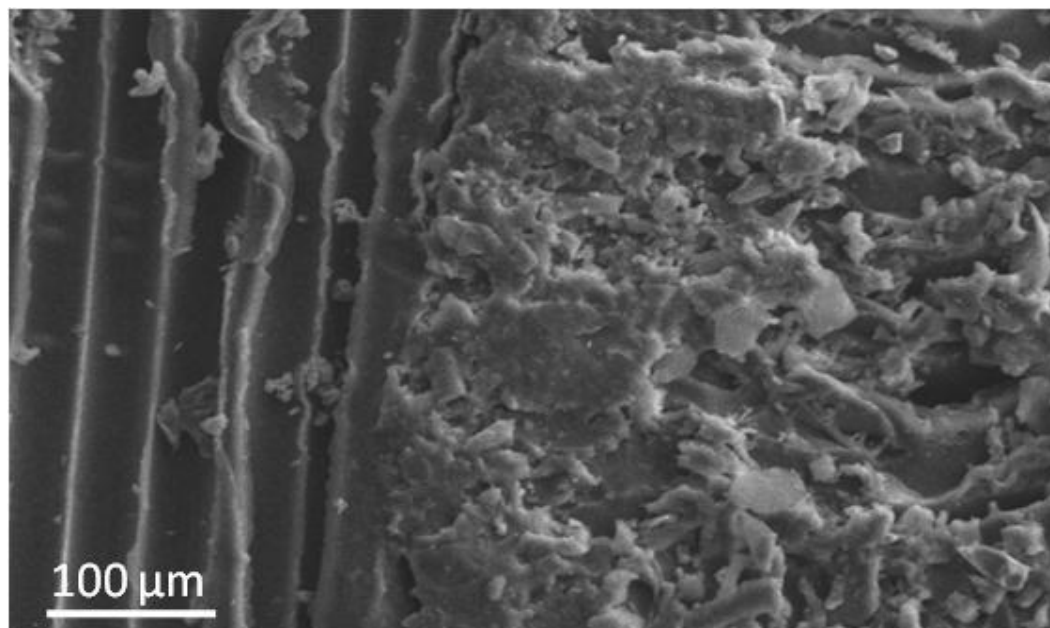
(b)



(c)



(d)



(e)

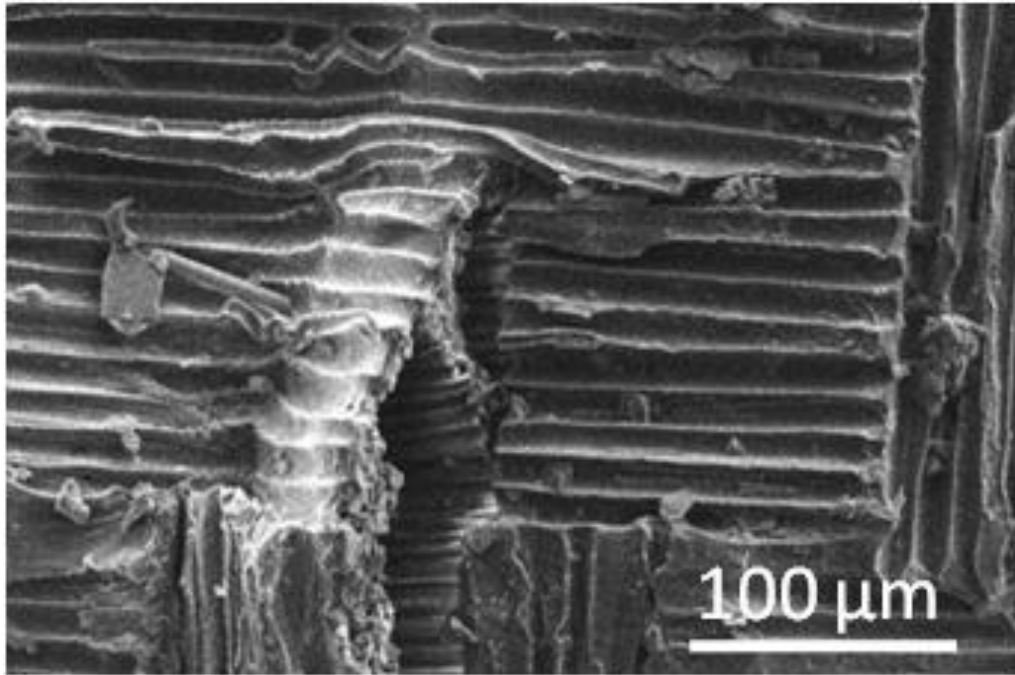


Figure 3.16: Fracture surfaces of: (a) EP GFRP (76% resin), (b) ACNT GFRP (76% resin), (c) PCNT GFRP (76% resin), (d) ACNT GFRP (69% resin) and (e) PCNT GFRP (69% resin)

On the other hand, it is known that PCNT samples have minimal interfacial adhesion with the fibres due to their inherent nature. As a consequence, on applying external load more matrix cracking and fibre debonding occurs throughout the interface. The presence of large sized clusters seen in Figure 3.16c is possibly fibre-matrix interface that got detached after a certain time interval during loading conditions. During that instance, the resistance to fibre-breakage by the glass fibres resulted in enhancing the flexural strength and ILSS properties of PCNT GFRP samples (as discussed previously).

Interestingly, the 3-D network observed in ACNT (amine-rich resin) sample (Figure 3.16d) provides a visual of the strong bonding between the modified matrix and the glass fibre that caused slower crack propagation and minimal pull-out of nanotubes which has been characterized by increased mechanical properties as mentioned in Table 3.1. In addition, careful examination of Figure 3.16d shows even more rough surface as compared to Figure 3.16b, which suggests the strong interfacial bonding between the amino groups on the surface of nanotubes and the epoxides of resin. The phenomenon of CNT bridging in CNT GFRP composites is in

agreement with the previously reported crack mechanism studies related to the CNT bridging effect [Gojny *et al.*, 2004b, Godara *et al.*, 2009]. On the contrary, Figure 3.16e clearly reveals rougher fibre surface as compared to Figure 3.16c and poor bonding between glass fibre sheets as evident from fibre debonding and pullout seen at several instances in the figure. Thus, SEM images support the failure mechanism as discussed previously and also weak fibre-matrix interface that resulted in early failure of PCNT GFRP (69% composition) samples under stress conditions.

From the above experimental results, it can be inferred that there are various parameters which affect the mechanical properties of the multi-phase composites. Parameters that possibly affect the mechanical behavior of nanocomposite materials are:

1. Resin content,
2. Processing techniques used to disperse CNT in an epoxy matrix,
3. Viscosity of the resin mixture during infusion,
4. Concentration of CNT in the matrix,

Out of these, the effect of modifying resin content on the mechanical properties has been discussed in detail in Section 3.4.1.3, while the effect of processing techniques and viscosity of resin mixture has been discussed in the following sub-sections. Since, the concentration of CNT was initially chosen as a constant in this research study, the effect of increasing CNT wt% in epoxy resin has been considered as a future scope.

3.4.1.4 Effect of processing techniques on dispersion of CNT in epoxy matrix

The polymer nanocomposites prepared using CNTs have shown remarkable mechanical behavior owing to the superior properties of the nanotubes when used as a secondary reinforcement in composite materials. The mechanical behavior of *in-situ* nanocomposites is dependent upon both the effective interfacial bonding between the individual constituents of the composite and on the dispersion of CNTs in the polymer matrix such as epoxy resin in this case. However, till date the full potential of CNTs as reinforcement is still limited primarily due to two reasons: non-homogenous dispersion of CNT as they exist as agglomerates and due to poor interfacial interaction between CNTs and the polymer matrix [Ma *et al.*, 2010]. Due to their high aspect ratio, particle – particle attractions and high surface area they tend to re-agglomerate with

time. However, there is an enormous amount of literature available on the techniques developed for CNT dispersion in polymer matrix [Mawhinney *et al.*, 2000, Shen *et al.*, 2004, Ma *et al.*, 2006, Ma *et al.*, 2007, Sham *et al.*, 2009] but none of them report a standardized method to overcome this major concern. Physical methods such as high-shear rate, sonication and milling while, chemical methods like the use of surfactants, solvents and chemical functionalization of CNTs can be used for obtaining efficient dispersion of CNTs in polymer matrices. Further, the literature strongly supports ‘Ultrasonication’ as an effective method to disperse CNTs in liquids having a low viscosity, such as water, solvents and few polymer matrices. In addition to this, mechanical stirring has also been considered as an effective tool to disperse nanoparticles in a polymer matrix. The size and shape of the propeller and the mixing speed controls the dispersion results. A study by May [May 1988] has reported a relatively fine dispersion of CNT in polymer matrix after intensive stirring. It is believed that by generating high mechanical forces, CNT agglomerates can be broken and homogeneous dispersion can be achieved. In order to produce high forces it requires the application of high-shear homogenizer at more than 15,000 rpm but studies pertaining to this are scant. High-shear homogenizer works on the principle that each time a fresh material is drawn into the work head, which continuously reduces them into smaller particle size and eventually results in a homogenous dispersion of the particles in the mixture. As the particle size reduces, carbon-carbon attractive force diminishes, which then reacts with the surrounding polymer matrix and form strong covalent bonds. Thus, it became interesting to investigate if mechanical stirring or high-shear homogenization would result in uniform dispersion of CNTs in the epoxy resin and a stabilized mixture i.e. without re-agglomeration of CNTs when kept for longer durations.

To explore the outcomes of two different stirring methodologies on the dispersion of ACNT in epoxy matrix, ACNT GFRP samples were prepared by following the two combinations: (i) mechanical stirring + ultrasonication and (ii) high shear homogenizer + ultrasonication. In brief, the PNC’s were prepared by adding 0.1 wt% ACNT in epoxy resin by using either homogenizer at a speed of 20,000 rpm or mechanical stirrer at 500 rpm. The resulting CNT/Epoxy mixture was sonicated at 40% amplitude for 10 min. These steps were repeated for one more time and then the hardener was added by using a mechanical stirrer. Finally, the polymer mixture was infused into the wax mold for fabricating CNT GFRP laminates which was later tested under both tensile and 3-point flexural bending mode.

Figures 3.17 and 3.18 illustrate the mechanical properties of ACNT GFRP samples prepared by above-mentioned techniques.

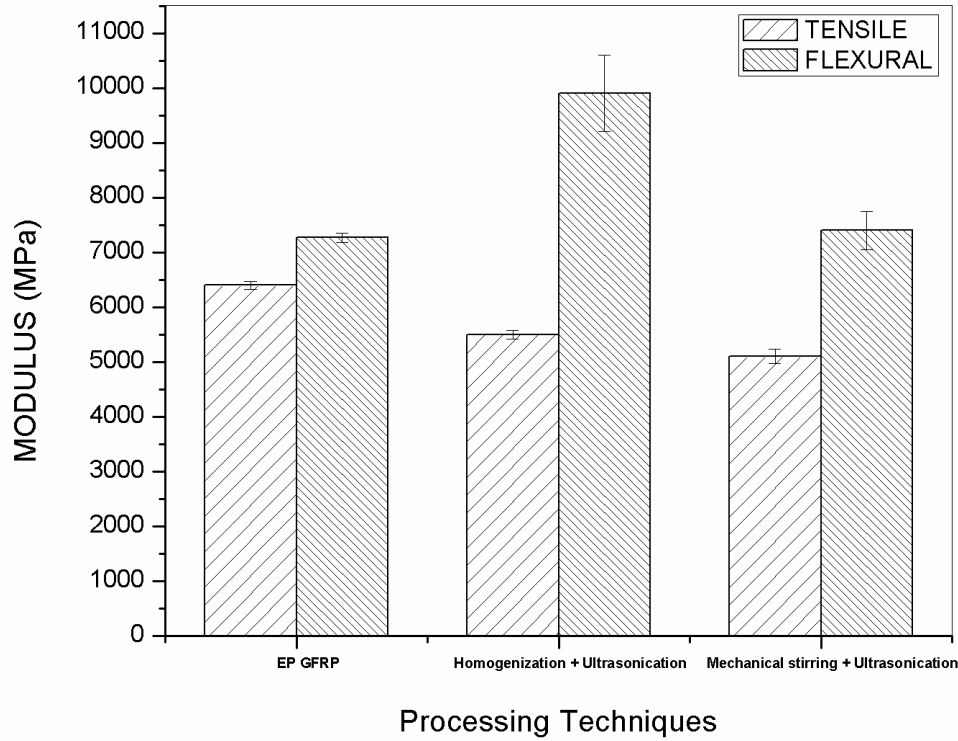


Figure 3.17: Effect of processing techniques on the modulus of CNT reinforced composites

It is clearly evident from Figures 3.17 and 3.18 that, for the samples prepared using mechanical stirring, flexural modulus and strength dropped by 25% and 29%, respectively, while the tensile properties are least affected as compared to high-shear homogenization samples. Since the composition of both the samples is same, it was expected that the tensile properties would not be altered much due to no-change in matrix composition. Furthermore, samples prepared using high-shear homogenization demonstrated an improvement of 36%, 45% and 39% in flexural modulus, strength and ILSS, respectively, while, flexural strength increased by only 3% on using mechanical stirrer, when compared with the EP GFRP sample. This suggests the poor mixing of ACNT in epoxy resin by using a mechanical stirrer at 500 rpm and possibly large CNT agglomerates acting as localized micro-structural defects which led to premature failure of the material. Hence, the dispersion of CNTs has revealed a significant effect on the fibre wettability and fibre-matrix interfacial bonding as evident from the change in flexural properties. The weak fibre-matrix interface was incapable of holding the external load for much longer and

thus resulted in deteriorated flexural properties, especially ILSS properties during flexural loading conditions.

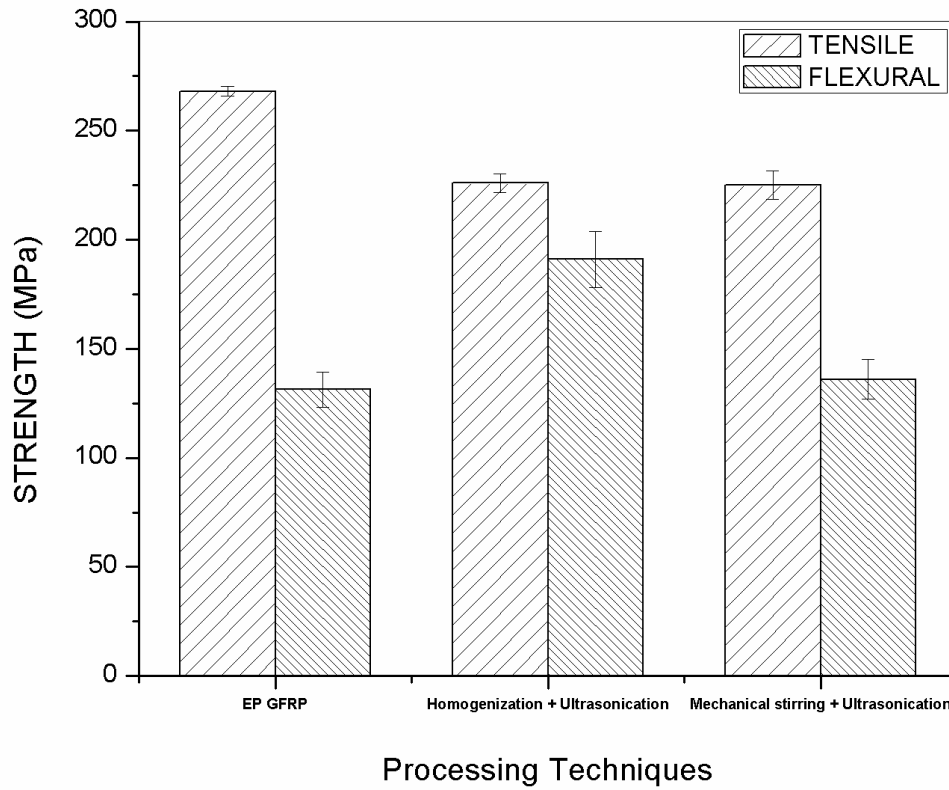
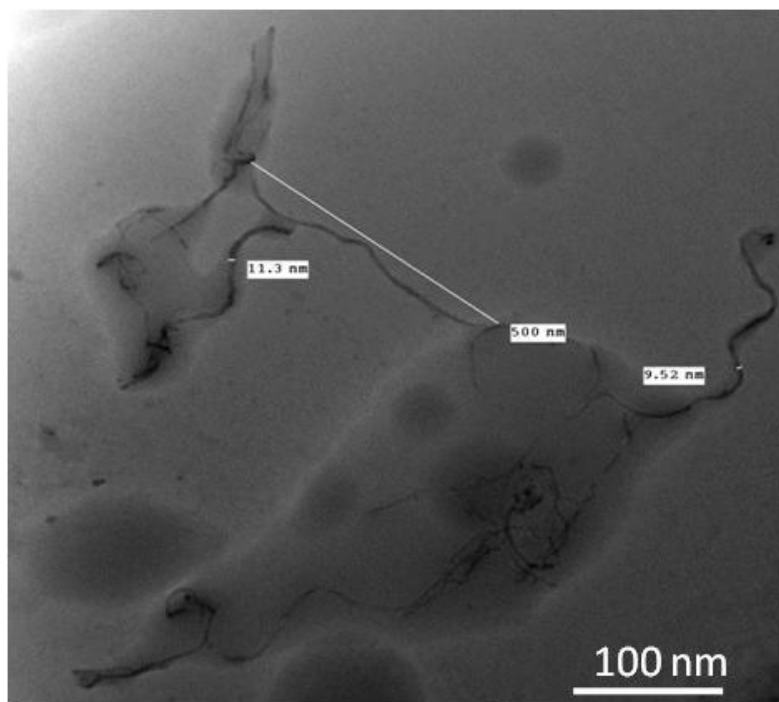


Figure 3.18: Effect of processing techniques on the strength of CNT reinforced composites

Therefore, homogenization has scored over conventional mechanical stirring technique with respect to dispersion and interfacial bonding issues faced with CNT nanocomposites. A possible reason for such behavior is that high-shear forces generated by homogenizer at 20,000 rpm were successful in breaking the nanotube agglomerates into smaller molecules. On using sonicator probe, these smaller molecules got enough energy to undergo a nucleophilic ring-opening reaction, which resulted in wrapping of polymers onto the CNT surface at an early stage of curing. This wrapped polymer acts as a protective layer and prevents re-agglomeration of nanotubes in the matrix. Thus, a strong interconnected network was formed as shown in Figure 3.19. The fibre-matrix interfacial adhesion is enhanced with CNTs and allows the load to be transferred between the two and at the same time, the gap between the highly mismatched properties of matrix and glass fibres is also bridged [Gojny *et al.*, 2005b].

(a)



(b)

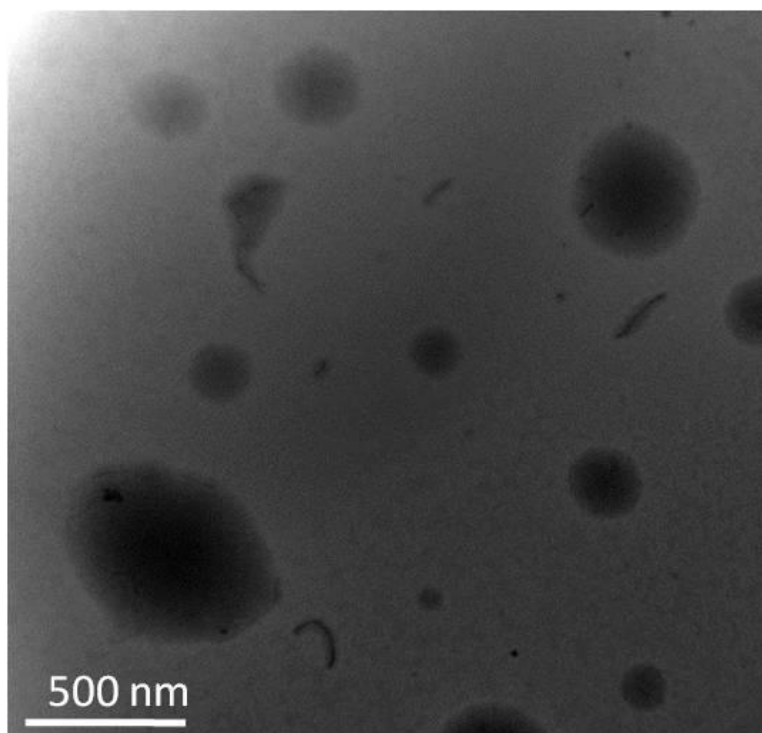


Figure 3.19: TEM images showing (a) dispersion of 0.1 wt% ACNT in epoxy resin, (b) homogeneous dispersion of ACNT in epoxy resin after sonication

Moreover, it is apparent from Figure 3.19a that ACNTs are well dispersed as single individual nanotubes and not bundled together. In addition to that, the aspect ratio (L/D) of ACNT is not significantly affected by implementing high-shear homogenizer and sonication processing techniques.

Thus, the uniform dispersion of ACNT in epoxy resin enables it to chemically react with epoxide groups and also allows it to act as fibres bridging the nano and micro-cracks in the matrix. Therefore, homogenous dispersion, strong interfacial bonding and high aspect ratio of ACNTs are believed to be the factors that caused the improvement in tensile and flexural properties vis-à-vis EP GFRP composites as observed in Figures 3.17 and 3.18. Hence, these experimental findings suggest the use of homogenization over mechanical stirring for dispersing CNTs in the epoxy resin and the same has been implemented for future experimental work.

The next goal of the present study is to investigate the effect of resin mixture temperature during infusion on the mechanical behavior of GFRP composites.

3.4.1.5 Effect of resin temperature during infusion on mechanical properties

During the processing phase, i.e. dispersing nanotubes in the resin by using sonication and homogenization techniques, temperature of the CNT/epoxy mixture was recorded after each step. It was observed that the temperature of the mixture after following the two-step approach (as described in Section 3.3.1.2) was about 60°C and subsequently, it lowered the viscosity of the mixture. It is known that the lower viscosity of the mixture is beneficial for both dispersion of nanotubes and fibre wetting. Hence, there seems to be a direct relation amongst the fibre wetting, adhesion strength and the mechanical performance of the composites. Therefore, to study this effect, experiments were carried out by raising the temperature of epoxy resin to 45°C from the recommended infusion temperature (i.e. 23 – 26°C) for two different GFRP compositions: (i) EP GFRP and ACNT GFRP as shown in Figures 3.20, 3.21 and 3.22.

Figure 3.20 clearly shows that as the infusion temperature is increased above the room temperature up to 45°C, it has a strong positive effect on the stiffness (modulus) specifically for EP GFRP composite samples while, for ACNT GFRP composites there was a slight drop in modulus values. Further, 98% improvement in flexural modulus, 182% in strength and 182% in ILSS is seen in Figures 3.20, 3.21 and 3.22, respectively for EP GFRP composites prepared at

45°C versus composites prepared at 25°C. Interestingly, this processing method has again revealed a significant change in flexural properties as observed by varying the processing technique (for details refer to section 3.4.1.4).

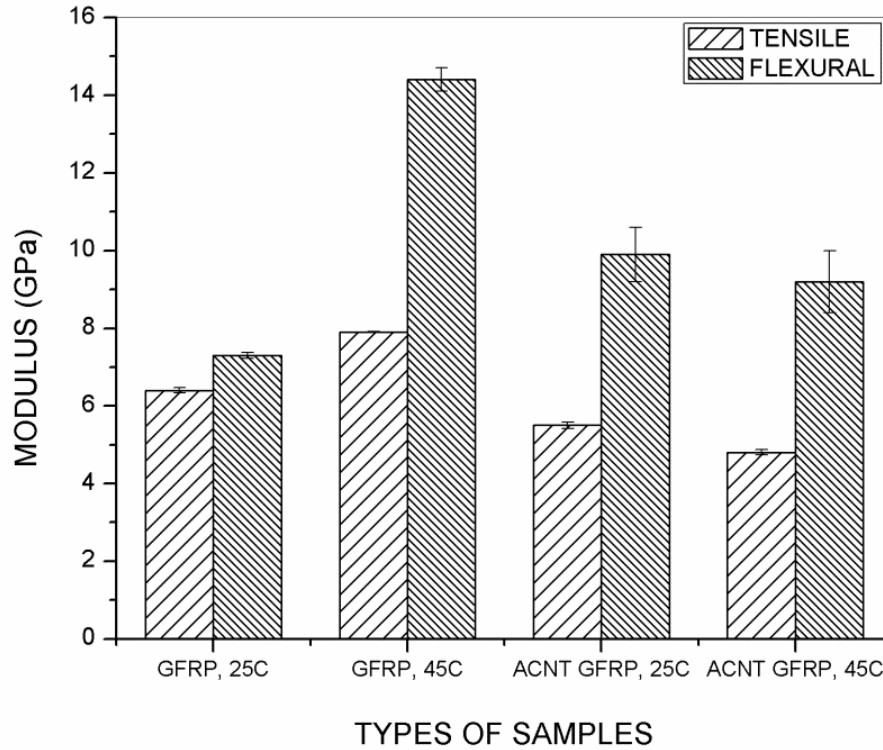


Figure 3.20: Effect of polymer mixture temperature on EP GFRP and ACNT GFRP composites: Modulus

On the other hand, ACNT GFRP samples manufactured at 45°C showed a slight improvement, i.e. 10% in tensile strength, 23% in flexural strength and 47% in ILSS properties vis-à-vis ACNT GFRP composites prepared at 25°C. This is certainly an interesting finding because at 25°C ACNT/Epoxy mixture was found to be highly viscous, likely due to the active attractive forces produced by extended π -electron systems between graphene layers of CNT surfaces; that results in re-agglomeration under certain conditions. As a result of which, there was poor wetting of the glass fibre sheets; it became difficult for the partially cross linked polymer molecules to conform to the fibre mat and infiltrate the inter-strand and inter-filament spaces. This led to increased porosity and defective sites in the resulting composites that eventually became the source of crack initiation under stress and the ultimate reason for the early failure of the composites.

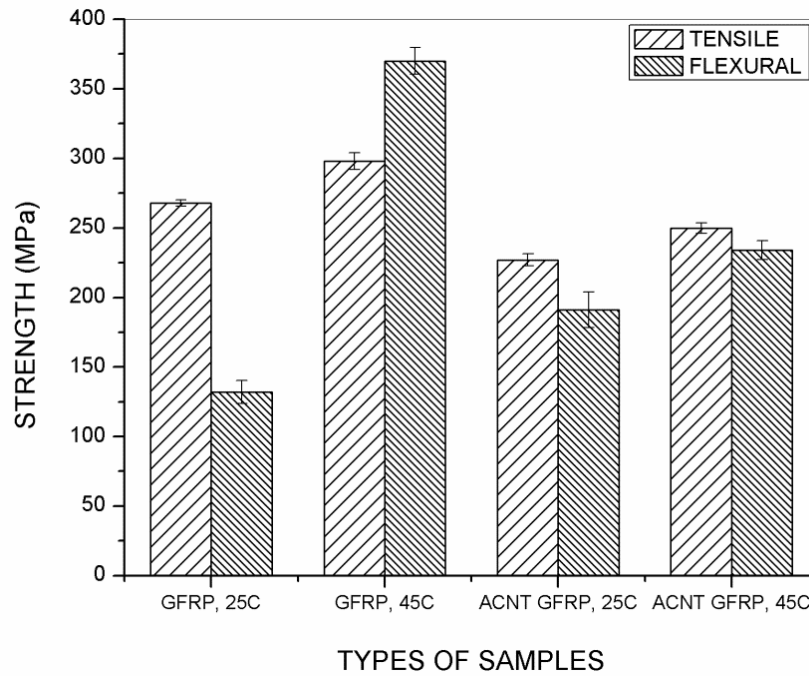


Figure 3.21: Effect of polymer mixture temperature on EP GFRP and ACNT GFRP composites: Strength

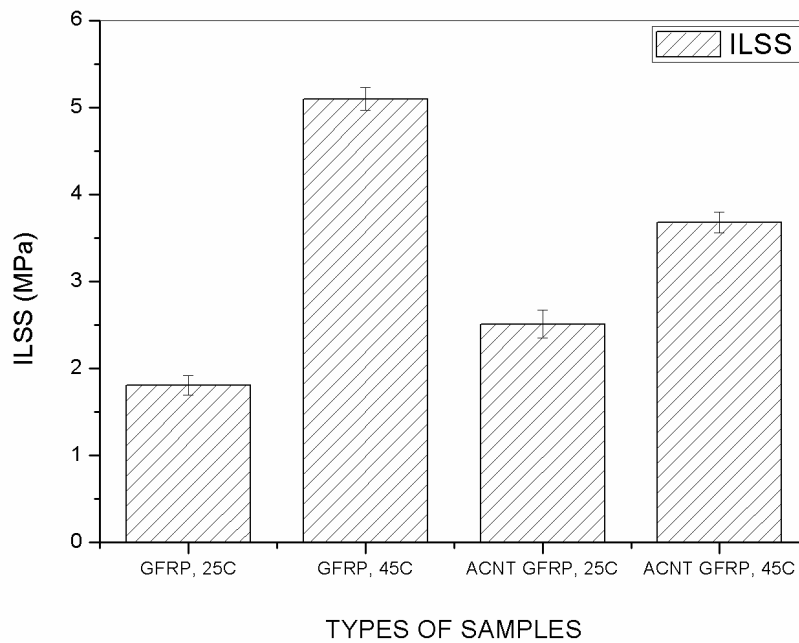


Figure 3.22: Effect of polymer mixture temperature on EP GFRP and ACNT GFRP composites: ILSS

In addition to this, it was found that there is an inverse relationship between the strain and modulus for ACNT GFRP samples prepared at 45°C and 25°C i.e. elongation at failure decreases while modulus increases by increasing the infusion temperature. The graph in Figure 3.23 clearly demonstrates that higher infusion temperature introduced brittleness in the composite behavior as compared to ductile failure at room temperature.

Therefore, the higher infusion temperature of the mixture has proven to be advantageous for EP GFRP specimens with respect to all mechanical properties while it is specific to few properties in the case of ACNT GFRP specimens. For that reason, the fabrication of polymer nanocomposites should certainly consider a higher temperature of the resin mixture prior to its infusion for curing mechanism and to obtain strong interfacial adhesion between the matrix and the glass fibres as per the findings from this experimental study.

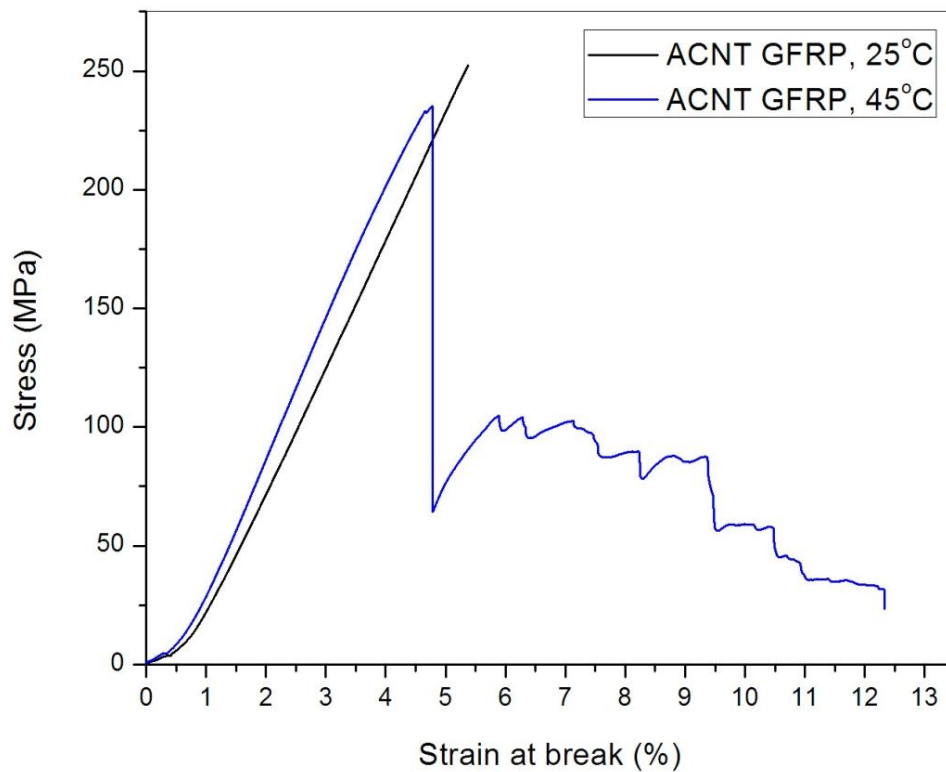


Figure 3.23: Effect of infusion temperature on stress versus strain relationship for ACNT GFRP composites

Hence, it can be concluded from the above discussion that various processing parameters affect the dispersion, interfacial bonding and the resulting mechanical properties of the

nanocomposites. The different parameters that influenced the performance of GFRP composites have been documented and taken into consideration for future experiments.

So far the goal was to enhance the dispersion and interfacial bonding by modifying the epoxy matrix at nanoscale. The objective of further strengthening the interfacial bond between the modified matrix and the glass fibres was possible by considering the use of silane coupling agents. The silane coupling agents could either be used for treating glass fibre mat or the nanotubes. Since the nanotubes being used in the present study are already modified, efforts were made to treat the surface of the glass fibre mat. The mechanical behavior of surface treated glass fibres in epoxy matrix has been discussed in the next chapter.

3.5 Closing remarks

Sonication and high shear homogenization processing techniques were able to effectively attain uniform and homogenous dispersion of carbon nanotubes in an epoxy matrix at a low loading level. The dispersion of ACNT in an epoxy resin demonstrated uniform dispersion as well as strong interfacial adhesion during the pre-curing phase of manufacturing glass fibre composites in VARIM. ACNT GFRP composites revealed considerable enhancement in tensile and flexural properties when prepared in an amine-rich resin matrix composition as compared to those obtained at stoichiometric ratio. Interestingly and contrary to popular perception, the present study reported higher mechanical properties for the composites with PCNT reinforcement in epoxy resin as compared to those with ACNT at stoichiometric ratio. Also, noteworthy improvement in mechanical performance was observed when the temperature of the resin being infused into VARIM mold was more than 40°C as compared to room temperature infusion. Besides this, TEM supported the uniform dispersion of nanotubes in epoxy, whereas SEM provided evidence for morphological changes in fibre-matrix interface due to reinforcement at nano-scale and lastly, FTIR analysis validated the chemical interactions between epoxy/hardener and nanotube/epoxy during the processing phase.

Chapter 4. Surface treatment of glass fibres

4.1 Introduction

In the last chapter, it was concluded that the use of high shear homogenization and ultrasonication techniques led to the homogeneous dispersion of ACNT resulting into their strong bond with epoxy resin. Thus, indicating strong interfacial adhesion which is further related to the enhanced mechanical performance of ACNT GFRP composites [Mallick 2007, Shen *et al.*, 2007b, Diez-Pascual *et al.*, 2011, Garg *et al.*, 2015].

Extending this study further, the next aim is to enhance the interfacial bonding between GF, epoxy matrix and CNTs. The surface treatments refers to a process during which glass or carbon fibres are subjected to different treatment such as exposure to high temperature and use of organosilanes. Exposing the fibres to high temperature in a muffle furnace during the initial stages removes the industrial fibre sizing from the as-received fibres. It is then subsequently replaced with an appropriate functional group on the fibre's surface as desired for the application. Interestingly, the literature also recommends the heat treatment of fibres in order to minimize the degradation of the glass fibre (GF) properties when exposed to harsh environmental conditions [Lee and Neville 1973, Ku-Herrera *et al.*, 2015] and hence, it has been chosen as one of the parameters in this work. Furthermore, the inorganic glass fibre surfaces are modified by using organosilanes such as silane coupling agents. The use of coupling agents results in a chemical interaction and aids in developing enhanced interfacial bonding between the fibres and the polymer matrix (such as epoxy resin in this case) [Park *et al.*, 2000, Zinck *et al.*, 2001, Iglesias *et al.*, 2002, Park *et al.*, 2003, Beg and Pickering 2006, Shokoohi *et al.*, 2008, Xie *et al.*, 2010, Isa *et al.*, 2014, Mahjouba *et al.*, 2014, Punyamurthy *et al.*, 2014, Tzounis *et al.*, 2014, Fiorea *et al.*, 2015, Ku-Herrera *et al.*, 2015, Nattapat *et al.*, 2015, Parida *et al.*, 2015]. The bridging mechanism so developed with high adhesion strength builds an efficient, stress transfer mechanism during the tensile and flexural loading conditions and demonstrates noteworthy improvement in material properties [Park *et al.*, 2000, Park *et al.*, 2004, Mehta *et al.*, 2006, Morales *et al.*, 2006].

Amongst the various silanes, aminosilane and glycidoxysilane, specifically 3-aminopropyltriethoxysilane (APS) and 3-Glycidyloxypropyltrimethoxy (GPS) are widely used for fibre surface treatment and as coupling agents for improving the fibre-matrix interfacial strength.

In this chapter, the fibre-matrix interfacial bonding with or without the presence of carbon nanotubes in EP GFRP composites, heat-treatment, and silane treatment of glass fibres with amino as well as epoxy silane coupling agents has been investigated. Also, their effect on the tensile and flexural properties, sub-surface behavior (morphology) and polymer interactions have been discussed in detail. Besides this, the dispersion of amino-CNTs in amine hardener has also been examined and the results were compared with those obtained by dispersing in resin. Lastly, for the purpose of manufacturing multiphase composites: a nanocomposite incorporating the best nano and macro-scale reinforcements, as determined independently, were blended to develop an optimal composite. The optimal composites stress-strain behavior under mechanical loading conditions was studied and the results have been presented in the chapter ahead.

4.2 Materials and Methodology

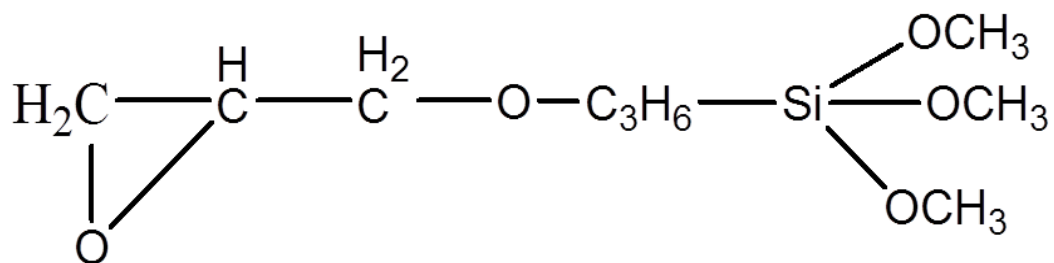
4.2.1 Materials

The silane coupling agents used for modifying the glass fibre surface with active chemical groups are: 3-Glycidyloxypropyltrimethoxy silane (referred to as epoxy silane, ES) and 3-Aminopropyltriethoxy silane (referred to as amino silane, AS) which were purchased from Tokyo Chemical Industry Co. Ltd., Japan, respectively. Absolute ethanol, methanol, acetone and glacial acetic acid were purchased from Sisco Research Laboratories Pvt. Ltd., India. All the chemical agents were of analytical grade and were used as-received without further purification.

4.2.2 Methodology

The chemical structures of epoxy and amino silane coupling agents incorporated in the present study are shown in Figure 4.1a and 4.1b, respectively.

(a)



(b)

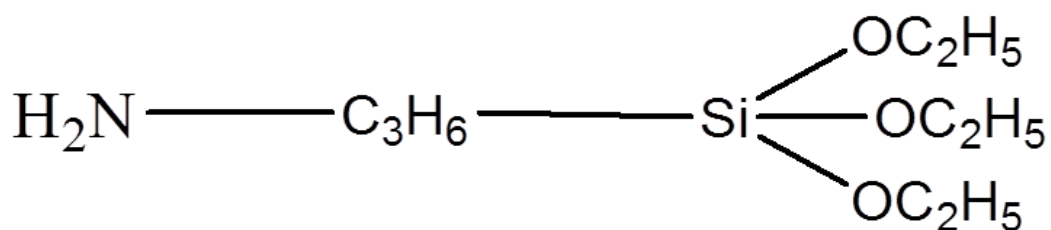


Figure 4.1: Chemical structure of (a) GPS and (b) APS silane coupling agents

4.2.2.1 Heat treatment

In order to carry out the cleansing and silane treatment of glass fibres, the fibre mat was heated up to 450°C for 1 h in a muffle furnace which also removes the commercial pre-sizing and organic compounds present on the surface of the glass fibre mat. Similar surface treatment of glass fibres prior to the composite fabrication was also carried out by Sever [Sever *et al.*, 2009]. In this study, both heat treated (HT) and as-received (AR) glass fibres were used. In order to further improve the fibre-matrix interface, the fibres (AR or HT) were treated with silane coupling agents. The chemical interaction of glass fibre surface with silane coupling agents has been illustrated using chemical equations as shown in Figure 1.5 (Refer to section 1.3). In general, when the glass fibres are dipped in silane solutions, the reactive silanols tend to form Si-O-Si bond among themselves and hydrogen bond with hydroxyls on the fibre surface. On heating, it promotes the condensation of free silanol groups which results in the formation of a solid siloxane layer on the fibre surface. Therefore, for the silane treatment of glass fibre mat, silane solutions were prepared by using ES and AS coupling agents, and their detailed preparation methodology is discussed ahead.

4.2.2.2 Epoxy silane treatment

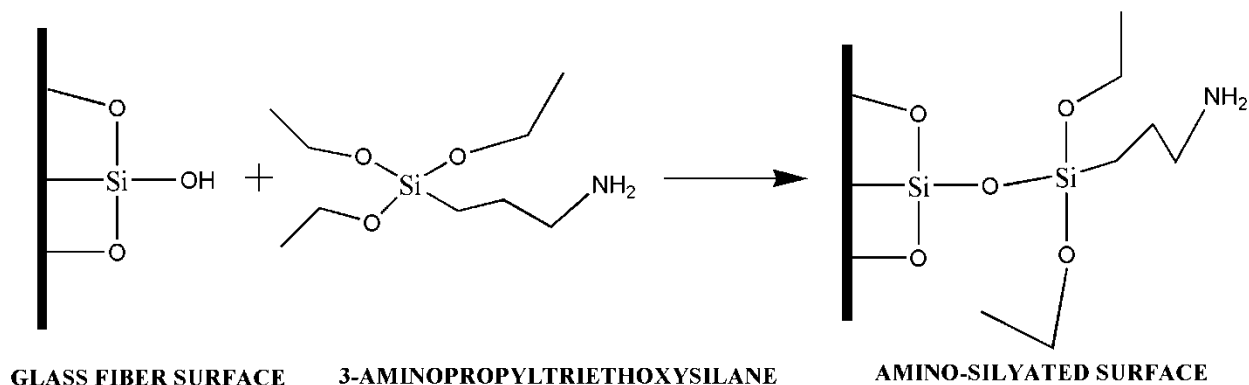
The ES treated fibres were obtained by the procedure reported in the literature [Gelset 2014]. The solution for ES treatment was processed by adding ES in a solution containing 95% ethanol and 5% distilled water while the pH of the mixture was maintained at 4.5 – 5.5 by using glacial acetic acid. The solution was manually stirred for 10 minutes to allow the self-condensation reaction to occur. The commonly used silane coupling agent concentration (specifically in commercial applications of glass fibre reinforcement) of 0.4 vol% was used in this experimental study as well. The silane agent was then added to the solution and stirred for 5 min. The glass fibres were immersed in the solution for 1-2 min and squeezed gently to remove any excess solution on the surface of the glass fibre mat. The fibres were then rinsed with ethanol to remove the excess solvent present on the glass fibre surface. Finally, ES treated glass fibre mats were air dried for 24 h.

4.2.2.3 Amino silane treatment

A similar procedure was followed for glass fibre surface treatment with an AS coupling agent. According to ThermoScientific [ThermoScientific 2014], acetone was used for AS treatment; and no pH adjustment was required since they are very stable in aqueous solutions as compared to epoxy silanes. The AS agent (0.4 vol%) was mixed with acetone solution and stirred for 5 min. The glass fibres were then dipped into the solution for 1-2 min and squeezed gently. This was followed by rinsing the wet glass fibre mat again with acetone and air drying at room temperature for 24 h. Lastly, the silane treated glass fibres were kept at 110⁰C for 5 min, prior to the fabrication process in order to complete the condensation of surface silanol groups and to remove any traces of chemicals used.

The mechanism of silane treatment with AS coupling agent has been depicted schematically in Figure 4.2a and the resulting siloxane cross-linked structure is shown in Figure 4.2b.

(a)



(b)

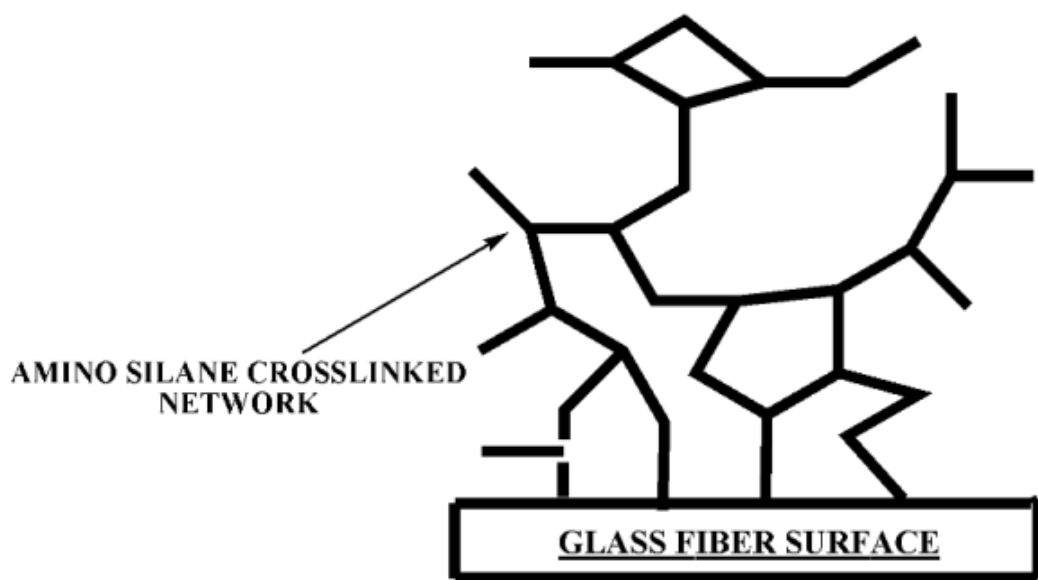


Figure 4.2: (a) Surface treatment of glass fibres with amino silane coupling agent; (b) schematic representation of a possible structure for amino silane coating on glass fibre

4.2.2.4 Characterization

The characterization of the prepared samples was done using the following equipments:

FTIR: This characterization (KBr pellet form) was carried out on Perkin-Elmer Spectrum using a transmission mode with a resolution of 4 cm^{-1} in the range of 4000 to 400 cm^{-1} .

SEM: The morphological characterizations of the fractured surfaces of the samples were examined in SEM (JEOL JSM 6510LV SEM at 20kV). All the specimens were prepared with a thin gold coating to avoid charging effects.

TEM: The TEM analysis was carried out on Hitachi (H-7500) operating at 110 kV. The fully sonicated liquid sample was placed onto a copper grid and observed under the microscope.

Mechanical testing: The tests for mechanical properties (i.e. tensile and flexural) were carried out on a Universal Testing Machine, Zwick Roell Z010. The tensile tests were carried according to ASTM D3039 at a crosshead speed of 2 mm/min while, the flexural tests were performed at a calculated speed of 1.34 mm/min (ASTM D790). Since the thickness of the specimen was less than 1.6 mm, the span-to-width ratio was kept at 25.4 mm as per ASTM recommendations. For each prepared composite, 4 samples were tested and average value has been reported.

However, for preparing advanced GFRP composites, the selection of silane coupling agent is a very critical and requires an in depth understanding of the bonding phenomenon. For that purpose, a rationale was brainstormed in order to decide the silane coupling agents which would be beneficial for manufacturing multifunctional glass fibre epoxy composites.

4.2.3 Rationale for choosing silane coupling agents

The first step involves the treatment of glass fibre mat with either AS or EScoupling agents and it is hypothesized that after drying it would result in either the presence of the active amino group or epoxide group on the surface of the mat. After the neat epoxy mixture is infused into the fibre sheets, these active groups would immediately undergo chemical reaction (as detailed in Figure 1.5) and build strong covalent bonds with the organic polymer resin

On the other hand, if CNT/Epoxy mixture is infused into silane treated glass fibres, it will possibly result in a more complex binding mechanism. The final CNT/Epoxy mixture prior to infusion in VARIM contains the epoxide group of resin, amino group of functionalized CNT and amino groups of the hardener. But, during the processing phase it was seen that epoxide groups of resin built strong covalent bonds with amino groups of CNT and probably left a few groups unreacted. Some of these readily available amino groups of CNT or epoxide group of resin will tend to form bonds either with the amine molecules of the hardener or active epoxy and amino

groups on the fibre surface. Thus, there seems to be two cases: one is interacting with ES GF and the other is AS GF.

Case I: If the glass fibre mat is treated with ES, the silanol groups at one end of the organosilanes will strongly hold to the glass fibre's surface, while the other end containing active epoxide group would be chemically active for further bonding. After the final CNT/Epoxy mixture is infused during fabrication into the ES treated glass fibre mat, the amino groups (few) of CNTs will tend to form covalent bonds with loosely available epoxide groups of the glass fibre mat. This would result in the bond formation between ACNT and glass fibre mat.

Case II: If the glass fibre mat is treated with AS, there is a strong possibility of having an already existing amino silane cross linked network (as shown in Figure 4.2) with several active amino sites present on the surface of the glass fibre mat. As the CNT/Epoxy mixture is made to interact with AS treated glass fibre mat it is assumed that the amino groups of CNTs and the glass fibre mat will not attract each other moiety due to their similar functional groups. As a result, no interactive bonding will take place between ACNT and the glass fibre mat and there would be excess amino groups available for bonding inside the composite interface. However, the amino silanol groups on the glass fibre mat would positively act as a nucleophile and form strong bonds with the epoxide group of resin and thus facilitate efficient stress-transfer mechanism. Subsequently, it has been reported earlier in this study that the amino groups of CNTs are covalently bonded to the epoxy matrix during its pre-curing phase. Overall, it would result in an inter-cross linked 3-D network amongst the epoxy resin, amino-CNTs and amino silane glass fibre.

But at the same instance, the fibre-matrix interfacial bonding seems to be a very complex mechanism while governing the mechanical performance of CNT reinforced glass fibre epoxy composites. An attempt has been made to design and understand this complex mechanism and is schematically represented in Figure 4.3. It lists the possible bonding that might occur and the strong covalent bonds formed during the processing of the matrix and the glass fibre mat. Firstly, a strong covalent bond is formed when resin is mixed with the hardener during its processing stage. Further, with the addition of amino-CNTs in a polymer matrix, the free amino groups react with the polymer molecules, expedite the curing process, result in stronger covalent linkage and improved bonding between the CNT and the matrix. The strong CNT-matrix bonding facilitates

the stress transfer during mechanical tests. When neat epoxy or CNT modified epoxy matrix is infused into AR glass fibres in VARIM, cure reaction tends to attain a fully cured polymer matrix. On the other hand, if EP mixture is infused into AS treated glass fibres, it is most likely to build a strong covalent bond with the amino molecules on fibre surface, thus improving the fibre-matrix interface. Similarly, freely available amino groups from either amino-CNT/Epoxy mixture or hardener will have a tendency to build stronger bonding with the ES on the fibre surface (due to their difference in basicity). However, the amino-CNTs may interact with amine hardener and/or AS GF sheets, showing an intricate behavior.

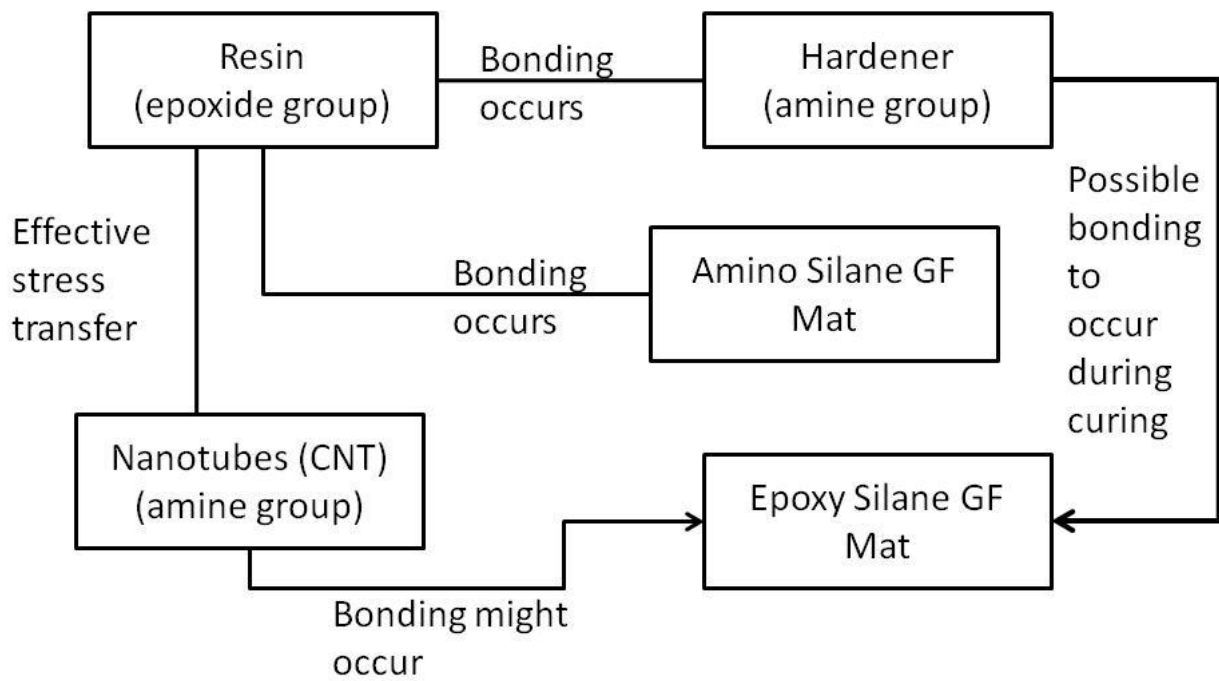


Figure 4.3: Schematic representation of the possible interactions among the various hybrid material constituents

Considering the possible chemical bonding illustrated in Figure 4.3, experiments were performed by incorporating silane treated glass fibre mats along-with various matrix compositions. However, prior to the silane treatment of glass fibre, heat treatment at a high temperature in a muffle furnace seemed advantageous to remove any commercial sizing and other organic impurities present. The present study is designed to explore the optimal conditions of silane treatment of glass fibre mat, for fabricating multifunctional GFRP composites which demonstrate enhanced mechanical properties, moisture and corrosion resistance specifically

suitable for marine structures. These composites were characterized for their chemical interactions, morphological changes and mechanical behavior.

4.3 Results and Discussion

A new manufacturing process that combined the two major reinforcements for fabricating polymer nanocomposites was studied. The proposed technique indicates the silane treatment of glass fibre surface along with the modification of epoxy resin with non-functionalized or functionalized CNTs. As discussed previously, heat-treatment of glass fibre prior to the silane treatment also might have a significant influence on the bonding strength and the same has been examined. A comparative investigation has been carried out for composites prepared using three different types of fibre mats in neat epoxy matrix and are listed below:

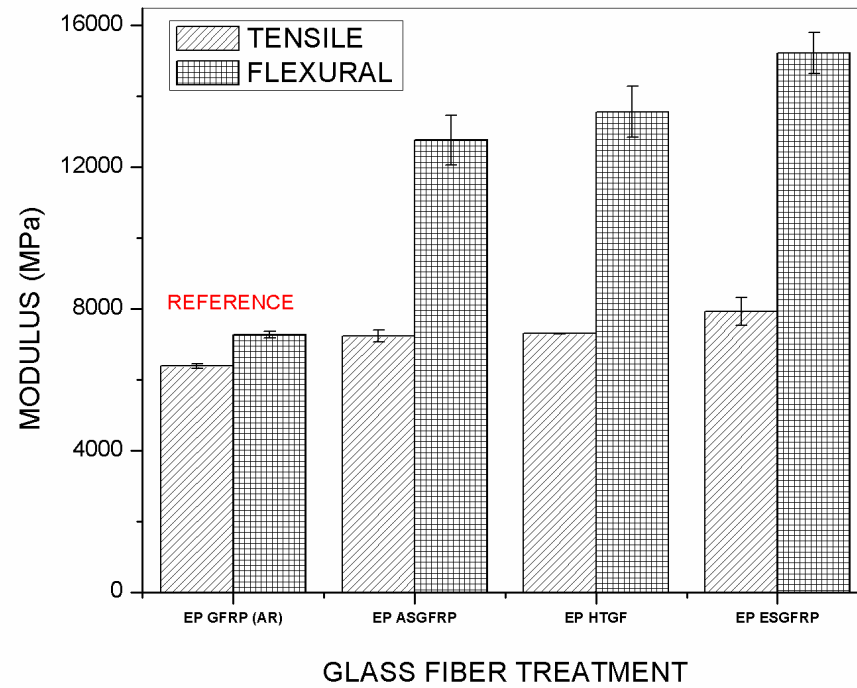
1. Neat or as-received (AR) glass fibre
2. Silane treated glass fibre (amino silane and epoxy silane)
3. Heat treated glass fibre (HT)

4.3.1 Mechanical behavior

To evaluate the mechanical response of silane treated glass fibre, AS and ES treated glass fibre mats were prepared without any prior heat treatment. The tensile and flexural results of these specimens are presented in Figures 4.4 (a and b). Interestingly, there is a considerable enhancement in the tensile and flexural properties for both AS and ES glass fibre treatments as compared to the AR glass fibre GFRP sample.

The silane treated glass fibres have shown higher Young's modulus under both tensile and flexural loading conditions as seen in Figure 4.4a. EP ESGFRP composites illustrate improved performance by 24% in tensile modulus and approximately 110% under the flexural conditions. Similarly, the EP ASGFRP sample showed an enhancement of 14% in tensile modulus and 76% in flexural modulus as compared to EP GFRP sample. The significant increase in flexural modulus for both silane treatments is likely due to the fact that the stress was transferred from the matrix to the fibres during the loading condition which is likely due to the presence of strong interfacial networking between treated fibre surface and the matrix.

(a)



(b)

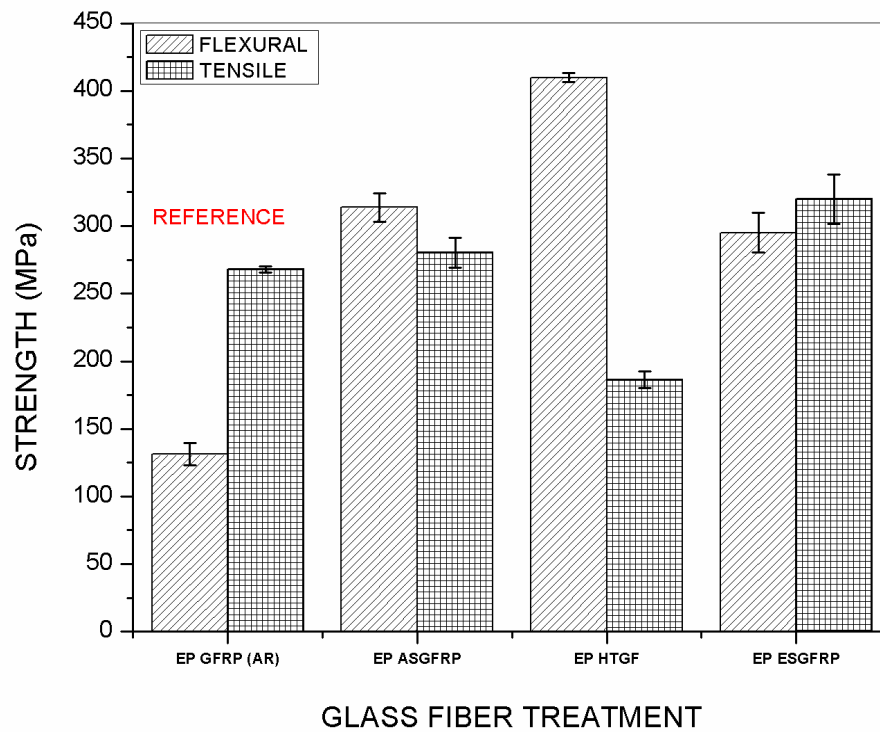


Figure 4.4: Effect of heat and silane treatment of AR glass fibre mat in neat epoxy on tensile and flexural properties studied through (a) modulus, (b) strength

Going further ahead, the analysis of HT GF has also proved to be beneficial during tensile (i.e. longitudinal) testing because, after heat-treatment the impurities and commercial sizing were removed considerably that provided additional numbers of active sites for bonding with resins.

Further, Figure 4.4b depicts the tensile and flexural strength for silane treated (AS and ES) and HT glass fibre composites. Evidently, flexural strength emphasizes on the adhesion between the epoxy matrix and the fibres. AS and ES treatments have shown a noteworthy enhancement in flexural strength by 139% and 125% respectively as compared to neat glass fibre composite that had a base strength of 131 MPa only. According to Wang [Wang *et al.*, 1999], the presence of active groups on the glass fibre surface (due to silane treatment) increases the flexural strength likely due to the existence of strong hydrogen bonding among the dissimilar phases.

In the present study, the experimental results indicate more than twofold i.e. 212% increase in flexural strength of HT glass fibre composites vis-à-vis neat glass fibre sample. A maximum value of tensile strength, i.e. 320 MPa was seen in the case of EP ESGFRP composite as compared to the EP GFRP composite which had strength of 268 MPa. The increased tensile and flexural properties (both modulus and strength) with silane treated glass fibre mats are possibly due to the stronger interfacial crosslinking network between the matrix and the glass fibre mat both being bonded to the two end groups of silane agent. Except for flexural strength, EP ESGFRP composites have depicted superior performance as compared to EP ASGFRP.

Therefore, one of the goals of proposed processing technique which is to build an efficient, stress transfer mechanism between glass fibre mat and polymer matrix seems to be attained by the quantitative and qualitative improvement in mechanical properties (as discussed above). From this study of three different fibre mats it has been observed that silane treatment works well with EP matrix, where the epoxy silane treatment seem to be of great advantage as compared to amino silane.

The next step of the research study was to observe the combined effect of two major reinforcements i.e. silane treatment of glass fibre mat and modified epoxy matrix with ACNT and PCNT. Additionally, the heat-treatment effect along with silane treatments (epoxy and amino) has also been reported in CNT modified matrix compositions. Furthermore, an interesting

comparison of the epoxy silane treatment of GF was performed using two different chemicals, i.e. methanol (M) and ethanol (E).

Firstly, the mechanical behavior in ACNT GFRP composition has been discussed, followed by PCNT GFRP composition. Figures 4.5 and 4.6 illustrate the experimental results of modulus and strength, respectively, of the composites tested where, ACNT GFRP (AR GF) composition was considered as a control specimen. The nomenclature represented in Figures 4.5 and 4.6 have been mentioned in detail in Table 4.1.

Table 4.1: Types of glass fibre treated samples in ACNT epoxy matrix

S.No.	Nomenclature	Type of sample
1	AR GF	As-received glass fibre (neat glass fibre)
2	AS(HT) GF	Amino silane and heat treated glass fibre
3	AS GF	Amino silane treated glass fibre
4	ES(M) GF	Epoxy silane with methanol treated glass fibre
5	ES(M,HT) GF	Epoxy silane with methanol and heat treated glass fibre
6	ES(E) GF	Epoxy silane with ethanol treated glass fibre
7	ES(E,HT) GF	Epoxy silane with ethanol and heat treated glass fibre

From the experimental findings, it can be stated that for AS treated glass fibre tensile and flexural modulus increased by 40%, 22% without prior heat treatment and increased to 75%, 35% with heat treatment, respectively, in comparison to the reference composite having a tensile modulus of 4.7 GPa and flexural modulus of 9.2 GPa. According to Schadler [Schadler *et al.*, 1998], in CNT/Epoxy composites, flexural modulus surpasses tensile modulus, demonstrating that during flexural loading all the nanotube layers are involved, whereas in tensile conditions

only the outer layer is extended. But, this trend was not observed in our experimental study since the tensile modulus was twofold that of the flexural modulus (being 40% and 20% and 75% and 35% respectively for tensile and flexural modulus).

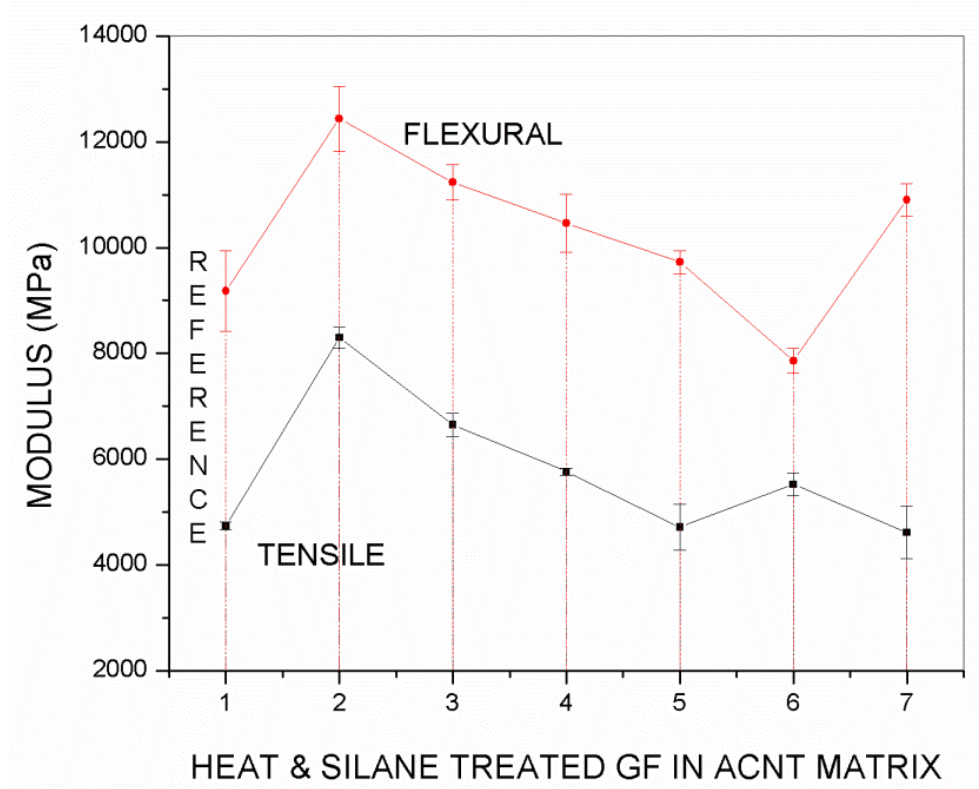


Figure 4.5: Effect of heat and silane treatment of GF in ACNT matrix on tensile and flexural modulus (1: ARGF; 2: AS(HT)GF; 3: ASGF; 4: ES(M)GF; 5: ES(M,HT)GF; 6: ES(E)GF; 7: ES(E,HT) GF)

Further, the observations from Figure 4.5 have been summarized by sorting the composites in decreasing order for the tensile and flexural modulus and listed in Table 4.2. The elasticity effect seems to increase significantly by both heat and amino silane treatment of glass fibre mat under both tensile and flexural loading conditions. Hence, the above results validate the hypothesis, i.e. amino silane glass fibre tends to build stronger covalent bonds with ACNT/Epoxy matrix. It has also been analyzed that tensile and flexural moduli are minutely affected by the various epoxy silane treatments. The epoxy silane-heat-treated GFRP composites

prepared with ethanol have shown better properties as compared to methanol as well as the control specimen.

Table 4.2: Trend of the silane & heat treated fibre mat in ACNT matrix composites for tensile and flexural modulus (decreasing order)

Highest	Tensile Modulus	Flexural Modulus
	AS (HT) GF	AS (HT) GF
	AS GF	AS GF
	ES (M) GF	ES (E, HT) GF
	ES (E) GF	ES (M) GF
	ES (M, HT) GF	ES (M, HT) GF
Lowest	ES (E, HT) GF	ES (E) GF

From Figure 4.6 it is evident that, the amino silane treatment of glass fibre mat has shown a remarkable effect on the strength in ACNT GFRP composites, causing a 33% increase in the tensile strength and 58% in flexural strength with only 0.4 vol% of amino silane coupling agent. This indicates that the amino silane glass fibre mat has built a highly cross linked network as it strongly holds the modified matrix during the loading conditions. Whereas, the incorporation of heat-treatment along with amino silane treatment has shown negligible effect on the tensile strength while, considerable (38%) increase in flexural strength.

After analyzing the results in Figure 4.6, it can be stated that tensile strength continues to decrease with different epoxy silane treatments of glass fibre in ACNT matrix composites with an exception for methanol treated glass fibre that showed an increase of 30%. Furthermore, the flexural strength has shown a better response with epoxy silane treatment of fibre mat, i.e. a maximum increase of 42% being reported for ES (E, HT) GF ACNT matrix composite as compared to the controlled composite. The effect of heat-treatment along with amino and epoxy silane treated glass fibre has shown an intricate behavior with respect to the mechanical

properties. In conclusion, the heat treatment of glass fibre needs to be studied in greater depth by taking care of other factors and hence forms an interesting topic for future endeavours.

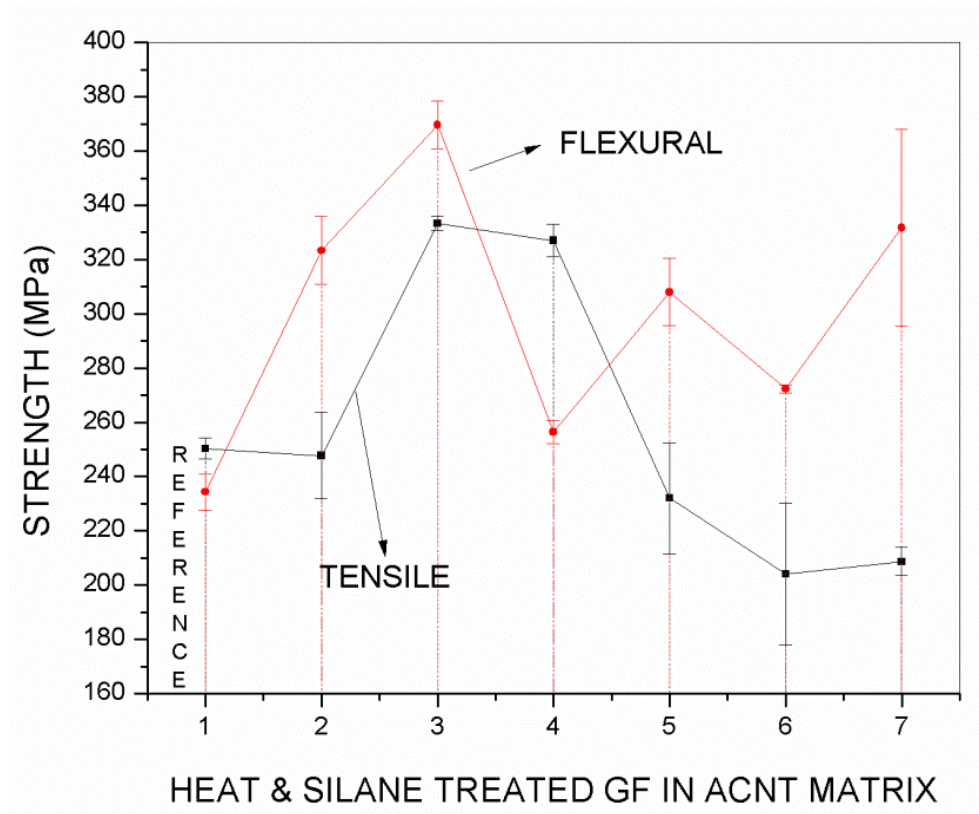


Figure 4.6: Effect of heat and silane treatment of GF in ACNT matrix on tensile and flexural strength (1: ARGF; 2: AS(HT)GF; 3: ASGF; 4: ES(M)GF; 5: ES(M,HT)GF; 6: ES(E)GF; 7: ES(E,HT) GF)

The presence of strong interfacial bonding between the silane treated glass fibre mat and epoxy resin has previously been confirmed by the experimental results discussed above. The next aim of the present study was to investigate specifically the silane treatment of glass fibre while, alleviating the effect of heat treatment in CNT modified epoxy composites.

To perform a qualitative analysis, comparison has been made for silane treated glass fibres in three different epoxy compositions: EP, ACNT and PCNT with details listed in Tables 4.3 and 4.4. Earlier in this study it was reported that ASGF mat showed a little enhancement in the mechanical performance when prepared with the EP composition. But, with the

reinforcement of ACNT in the epoxy matrix it showed a qualitative improvement by 19% in tensile strength and 18% in flexural strength vis-à-vis ASGF/neat epoxy composite.

Table 4.3: Tensile and flexural properties of amino silane treated GF in different epoxy matrix compositions

S.No.	Specimen	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)
1.	EP ASGFRP	7.2 ± 0.17	280 ± 10.9	12.7 ± 0.70	314 ± 10.6
2.	ACNT ASGFRP	6.7 ± 0.22	333 ± 2.7	11.2 ± 0.34	370 ± 8.8
3.	PCNT ASGFRP	6.1 ± 0.22	341 ± 3.5	12.5 ± 0.35	349 ± 30.2

Hence, it can be assumed that there exists a stronger interfacial bonding between the amino groups of nanotubes, epoxy matrix and the amino silane treated glass fibre, as seen in Figures 4.2 (of section 4.2.2.3) and also evident from improved mechanical behavior of ACNT reinforced composite (as discussed in Chapter 3). On the other hand, the tensile and flexural strength for PCNT samples (row 3 in Table 4.3) has also significantly improved vis-a-vis EP ASGFRP composition (row 1 in Table 4.3). It is possibly due to the strong interface adhesion between AS glass fibre and epoxy matrix [Godara *et al.*, 2009, Anas *et al.*, 2013]. However, by looking at column 6 of Table 4.3 it is evident that ACNT ASGFRP composite has scored over both PCNT and EP ASGFRP composites.

Therefore, experimental results highlight the fact that there existed a strong cross-linking network between the amino groups (of CNTs, hardener and glass fibre) and an epoxide group of resin, thus validating the homogenous and uniform dispersion of ACNT in epoxy matrix by the chosen processing techniques. As a result, during testing conditions, the stress was transferred efficiently from the matrix to the nanotubes, observed in terms of improvement in mechanical behavior of the composite. From the experimental and theoretical findings, it is affirmative that amino silane molecules on the glass fibre surface forms a strong fibre-matrix interface

irrespective of the nanofiller chosen that consequently inhibits the mobility of the polymer matrix and results into enhanced tensile and flexural properties of the composites as observed experimentally.

Table 4.4 shows the results of EP ESGFRP reinforced with ACNT and PCNT nanotubes. The results suggest that PCNTs have shown better strength properties in ESGF as compared to the EP and ACNT samples. Exclusively, it has been observed that for PCNT composites (refer to row 3 in Table 4.4) the tensile and flexural strength increased from 320 MPa to 369 MPa and from 295 MPa to 337 MPa, respectively as compared to EP ESGFRP (row 1 in Table 4.4). Also, the mechanical performance of PCNT ESGFRP has scored over ACNT ESGFRP composite for all the mechanical properties studied, which implies that there is an improvement by 7.3% in tensile modulus, 81% in tensile strength, 72% in flexural modulus and 24% in flexural strength.

Table 4.4: Tensile and flexural properties of epoxy silane treated GF in different epoxy matrix compositions

S.No.	Specimen	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)
1.	EP ESGFRP	7.9 ± 0.38	320 ± 18.2	15.2 ± 0.58	295 ± 14.6
2.	ACNT ESGFRP	5.5 ± 0.21	204 ± 26.1	7.9 ± 0.24	272 ± 1.5
3.	PCNT ESGFRP	5.9 ± 0.02	369 ± 7.3	13.6 ± 0.69	337 ± 28

Such results are possibly due to the interconnected network between epoxy groups on a glass fibre mat and epoxide of resin with amine hardener. Another possible reason for the distinguished behavior of PCNT over ACNT in ESGF composites is due to the greater aspect ratio of PCNT than ACNT. The non-functionalized nanotubes i.e. PCNT have length closer to 1 micrometer whereas the length of ACNT is shortened during its functionalization process, that involves the use of highly concentrated acids, which results in the shortening of its length. It is possible due to this reason that pristine nanotubes were able to effectively handle the internal

stresses induced during stretching or bending mode and resulted in much better mechanical response.

4.3.2 FTIR and SEM analysis

Characterization techniques such as FTIR and SEM have also verified the chemical interaction and presence of interfacial adhesion between the ACNT/Epoxy matrix and amino silane treated glass fibres.

Figure 4.7 illustrates the chemical interaction between CNT modified epoxy matrix and silane treated glass fibres characterized through FTIR analysis. FTIR of ACNT ARGFRP and ACNT ASGFRP composites are shown in Figure 4.7. It can be clearly seen that the spectral bands are quite similar, except that there is a shift in some peaks and also the intensity of transmittance is observed to be higher at some wavelengths. Figure 4.7a shows the FTIR spectra of the ACNT ARGFRP composite and it indicates that ACNT has undergone a chemical reaction with the epoxy matrix, since the epoxide ring bands are missing from this spectrum at $800\text{-}920\text{cm}^{-1}$ [Baudot *et al.*, 2010]. On comparing, the FTIR spectrum for the uncured epoxy, as depicted in Figure 3.8a, with that shown here in Figure 4.7a it is observed that for pristine epoxy the maximum absorption intensity of the band is around 915 cm^{-1} while the same diminishes as the chemical reaction progresses for ACNT GFRP composites.

Figure 4.7a also shows the C-N stretch (primary amine) in the range of $1090\text{-}1020\text{ cm}^{-1}$. However, as the curing reaction proceeds between the ACNT and the epoxy resin, the primary amines are utilized by the epoxide groups resulting in the formation of secondary and tertiary amines. The secondary and tertiary amines can also be identified in the FTIR spectra. On carefully analyzing the two spectra in Figure 4.7a, the absorption bands in the range $3430\text{-}3490\text{ cm}^{-1}$ represent heterocyclic amine, N-H stretch [Garg *et al.*, 2011, Ma *et al.*, 2010]. Additionally, the sharp peak at 1182 cm^{-1} refers to the presence of C-N stretch due to the formation of secondary amine [Garg *et al.*, 2011]. The presence of N-H bends due to secondary amine has been verified by the peaks in the range of $1650\text{-}1550\text{ cm}^{-1}$ [Garg *et al.*, 2011] as shown in Figure 4.7a.

Figure 4.7b shows the spectra of ACNT ASGFRP composite. FTIR spectra of a silane treated polymeric composite proved the formation of Si-O-C bonds and also Si-O-Si bonds that resulted due to silanization mechanism.

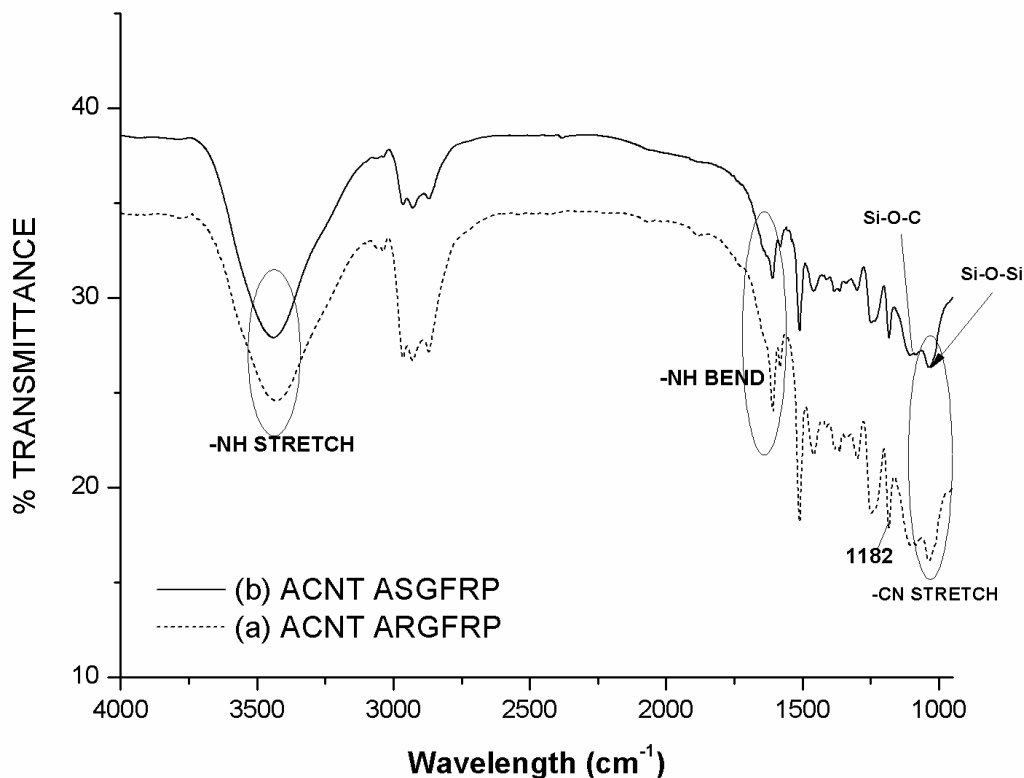


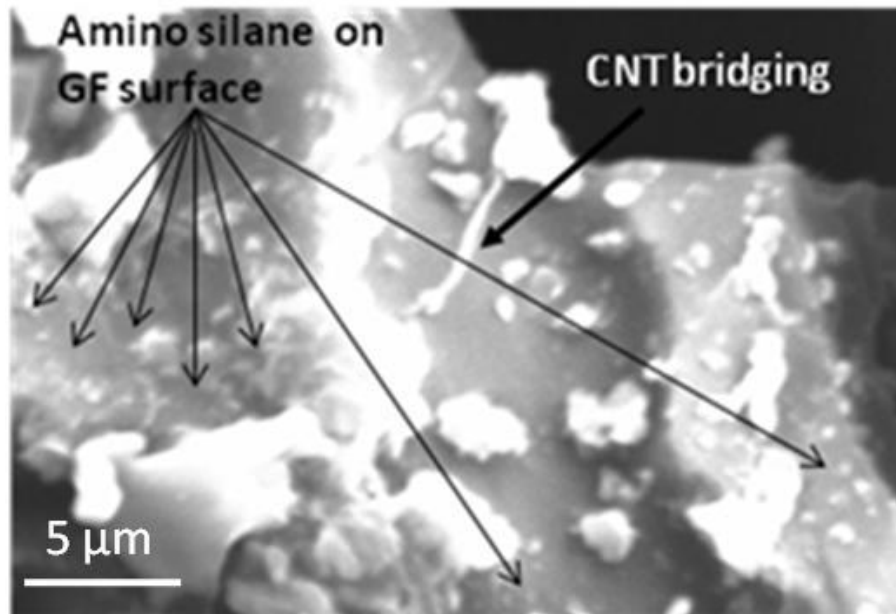
Figure 4.7: FTIR spectra of ACNT ASGFRP composite (shown by solid line) and ACNT ARGFRP composite (shown by dotted line)

The two major bands observed in this spectrum are at: 1105 and 1036 cm⁻¹ which illustrates the presence of organic siloxanes in the composites. These bands were detected most likely due to the fibre modification with an amino silane coupling agent. The band at 1105 cm⁻¹ signifies the Si-O-C linkage between the silane molecules and the epoxide group of resin. Interestingly, when the silanols do not react with glass fibre surface, they tend to condense themselves, resulting in the formation of Si-O-Si bonds on the surface of the glass fibre and these have been observed at 1036 cm⁻¹ in FTIR spectrum. Moreover, the intensity of transmittance of primary amine in the range 3430-3490 cm⁻¹ has also increased as seen in Figure 4.7b which is likely due to the presence of excess amino groups present in the polymer composite and

transmitted from silane treated glass fibre mat. Therefore, the FTIR results confirmed an existence of bonding between ACNT, silane treated fibre surface and the epoxy matrix.

SEM images also support the quantitative results obtained through mechanical testing. Figures 4.8 (a and b) show the SEM images of the fractured samples of ACNT ASGFRP and ACNT ESGFRP, respectively. Generally, on observing the surface of as-received glass fibre epoxy sample, a clear and smooth surface embedded in an epoxy matrix appears. But, in Figure 4.8a rough surface was observed that is due to the presence of amino silane particles on the glass fibre surface. These silane particles formed strong covalent bonds with epoxy resin, and thus resulted in improvement in the tensile and flexural properties of the prepared multiscale composites as listed in Table 4.3. The reinforcement of epoxy matrix with the addition of carbon nanotubes possibly assists the postponement of crack initiation or hinders the crack propagation either by deflection or crack bridging. The CNT-bridging observed in fractured samples (Figure 4.8a) for crack propagation region illustrates the strong bonding between the ACNT, epoxy matrix and the glass fibre mat. The extensive CNT bridging observed in the SEM image (Figure 4.8a) is in agreement with the previously reported crack mechanism studies [Schadler *et al.*, 1998, Godara *et al.*, 2009, Gojny *et al.*, 2004b, Zhou Y *et al.*, 2007].

(a)



(b)

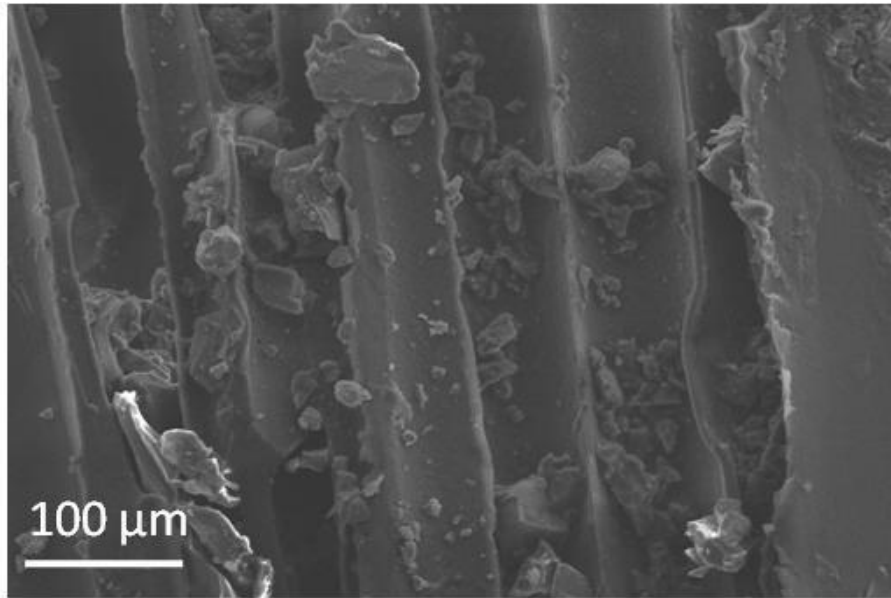


Figure 4.8: Fracture surface of (a) ACNT ASGFRP, (b) ACNT ESGFRP samples

On the other hand, the surface of ES GF/ACNT composites (as shown in Figure 4.8b) demonstrates a weak fibre-matrix adhesion, leaving a number of traces of clearly pulled out fibres behind, thus validating the deteriorated mechanical behavior of the composites as discussed earlier. Furthermore, a greater extent of matrix cracking on the fibre surface was seen after mechanical tests as compared to neat glass fibre epoxy sample. Hence, it can be stated that crack initiation and propagation becomes complicated in CNT modified epoxy laminates.

In conclusion, ES treated glass fibre mat in neat epoxy matrix showed considerable improvement as compared to AS treated glass fibre. Additionally, the effect of ES and AS treated glass fibre in the presence of PCNT and ACNT nanotubes was also explored. The experimental findings demonstrate that AS shows strong interfacial adhesion in ACNT matrix whereas, ES shows improved mechanical behavior in PCNT matrix. So far, it was assumed that in order to attain uniform dispersion and to build strong nanotubes/matrix interface, CNTs should be dispersed only in epoxy resin and successful results have supported this assumption. But, considering the findings from the last section and possible interactions represented in Figure 4.3 it seemed feasible to explore the mechanical behavior by dispersing amino-CNTs in hardener as compared to epoxy resin.

4.3.3 Effect of ACNT dispersion in amine hardener versus resin

The hardener chosen in the present study consists of amine molecules attached to both ends of poly(oxypropylene) moiety and is of lower viscosity than epoxy resin. These features/characteristics of the hardener seemed to favor the dispersion of amino-CNTs. Interestingly, studies have also been carried out in the past where CNTs were initially dispersed in the hardener using processing techniques such as sonication, shear-mixing or calendaring [Gojny and Schulte 2004a, Kim *et al.*, 2009] and stated that the best dispersion was achieved by suspending the nanotubes in the hardener.

To investigate this phenomenon, 0.1 wt% ACNT of the total mixture was added to the hardener using a high-shear homogenizer at 10,000 rpm for 5 min followed by probe sonication set at 40% amplitude for 10 min. A lower rpm (as compared to previous 20,000 rpm) for homogenizer was chosen due to the low viscosity of curing agent. The resulting mixture was kept in desiccator under vacuum for 1 h to remove any entrapped air. The stoichiometric ratio of resin was then added using a mechanical stirrer at 500 rpm for 5 minutes. The resulting mixture was then infused into neat glass fibres using VARIM to prepare a laminate under controlled conditions.

Table 4.5 presents a summary of the percent change in mechanical properties obtained for ACNT/hardener GFRP composite as compared to ACNT GFRP composite and EP GFRP composite. In brief, the tensile strength demonstrated approximately 40% increase as compared to ACNT GFRP, while it showed more than 50% enhancement in flexural strength and ILSS as compared to EP GFRP sample. Especially, the tensile properties demonstrated significant improvement over flexural ones, which highlights the fact that nanotubes have been beneficial in enhancing the covalent bonding between the matrix and nanotubes which further facilitated load handling capability of the composite material. On the other hand, the fibre-dominated properties showed modest improvement. A possible explanation of such behavior is that: after the dispersion of amino-CNTs in the amine hardener there was a tendency to build ionic bonds between themselves, due to the same polarity, and thus formed a long polymeric chain. This polymer chain had excess amino groups present and as the epoxy resin was added using mechanical stirring, a nucleophilic ring-opening reaction occurred between the epoxide and amino groups which resulted in the formation of a long, strong interconnected amine-epoxide

chain. In addition to that, the formation of strong covalent bonds between the amino-CNTs and the resin further improved the nanotubes/epoxy resin interface, developed an effective stress transfer mechanism and thus enhanced the mechanical properties.

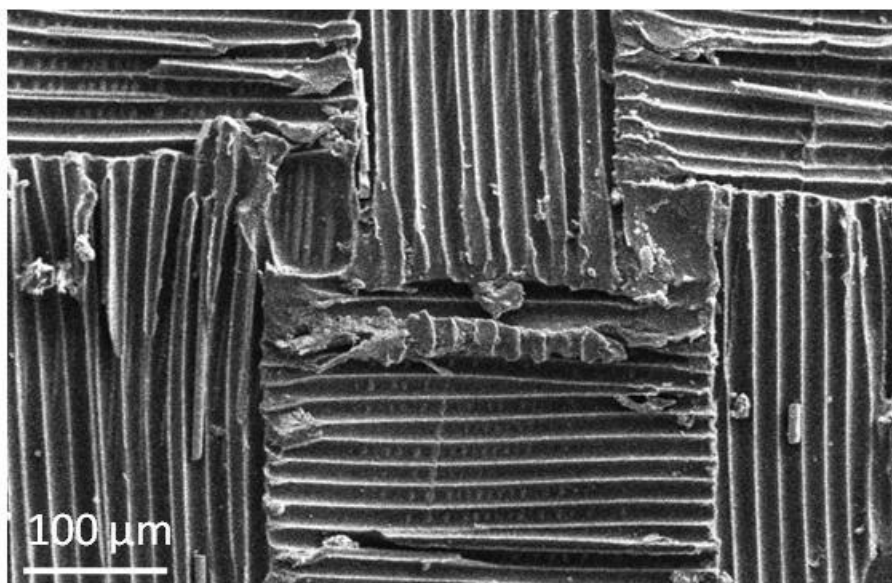
Table 4.5: Comparison of the mechanical properties for ACNT/hardener GFRP composite

Property	% improvement as compared to ACNT GFRP	% improvement as compared to EP GFRP
Tensile modulus	30 % increase	11 % increase
Tensile strength	42% increase	20 % increase
Flexural modulus	6.8 % decrease	27 % increase
Flexural strength	6.1 % increase	54 % increase
ILSS	12 % increase	55 % increase

Since, the mechanical test results were quite motivating it was essential to compare the morphological changes as well. Figure 4.9 compares the SEM images of ACNT/Epoxy and ACNT/hardener GFRP samples. From Figure 4.9a, it is clearly visible that the bi-directional layers of the glass fibre mat have a coarse surface. The surface appears to be dense and compact with unbroken CNTs still adhering to the matrix, thus suggesting comparatively stronger interfacial bonding between the resin and the amino- CNTs. On the other hand, Figure 4.9b shows even dense surface, i.e. the fibres were completely covered by the epoxy matrix. Moreover, it can be seen that even after the application of compressive stress, the fibre direction remains unaffected and only minimal fibre pull-outs are observed. Interestingly, the SEM image did neither show smooth surface nor a fracture pattern that provides evidence for crack initiation. Similar fracture surface behavior by suspending ACNT in the hardener has also been reported by Gojny [Gojny and Schulte 2004a]. Generally, it is observed that an application of stress on the composites, the fibres tend to break and appear as broken pieces as seen in Figure 4.9a. This has not been observed for ACNT/hardener samples (Figure 4.9b) certainly due to the existence of strong bonding between the matrix, glass fibres and the nanotubes, which further assisted in

handling stress during mechanical tests. Hence, the outstanding mechanical behavior seen by dispersing amino-CNTs in the hardener seems to be well justified.

(a)



(b)

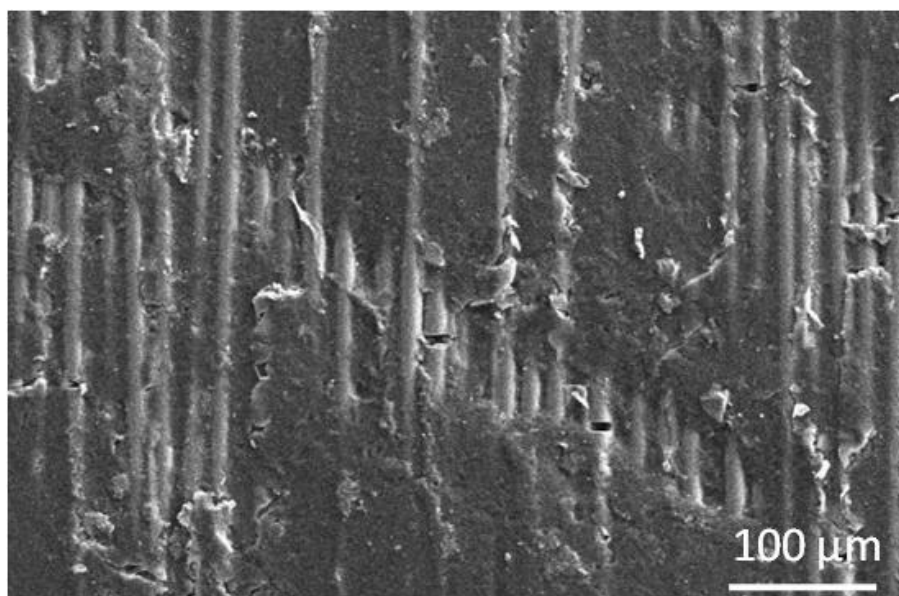


Figure 4.9 : SEM images of (a) ACNT dispersion in resin and (b) ACNT dispersion in hardener

The study carried out till now has been successful in maximizing the mechanical behavior for the epoxy matrix and glass fibres individually by varying several different parameters. But, considering the requirement of developing a multifunctional composite material it was vital to incorporate the optimal conditions for the major constituents of a composite i.e. the matrix and the fibres.

4.3.4 Composite with optimal matrix and silane treatment

For the purposes of preparing a multifunctional composite material, the findings from the CNT and silane treatment of glass fibre investigations were blended together. Therefore, a composite was prepared with the dispersion of 0.1 wt% ACNT in an amine-rich epoxy resin system by using sonication and high-shear homogenization techniques. After the homogeneous dispersion of ACNT in the epoxy, the mixture was kept in vacuum for 2 h followed by the addition of hardener in the ACNT/Epoxy mixture. In addition to that, the temperature of the final mixture was controlled at nearly 40°C since it resulted in better wetting of the glass fibres. On the other hand, the experimental results discussed above clearly demonstrated better interfacial adhesion of amino silane fibres with ACNT than PCNT, and hence chosen for this fabrication. Lastly, the amino-silane treated glass fibres were infused with ACNT/Epoxy mixture and cured for 7 h at 70°C under controlled vacuum conditions in VARIM.

It is necessary to point out that this composition differs from the previous sections as those composites were prepared at the stoichiometric ratio, while the former is being manufactured in an amine-rich resin composition. After their fabrication, the samples were mechanically tested and their results have been listed in Table 4.6 along with EP GFRP samples. Also, the percent change in mechanical properties as compared to EP GFRP samples has been represented by the ($\pm$) values along with their actual experimentally determined ones.

In general, by analyzing column 4 in Table 4.6, it is evident that flexural properties have shown much higher improvement as compared to its tensile behavior. The surface treatment of glass fibres with amino silane possibly built a strong amino interconnected network with fibres on one side while, the other end strongly holds to the epoxy matrix. Thus, when the samples were subjected to flexural loading conditions, the CNT reinforced matrix sustained the load for a long time and probably transferred minimal stress to the glass fibres. As a result, it prevented

crack initiation and growth, debonding of glass fibres and fibre failure, which was apparent by enhancement observed in flexural strength and interlaminar shear strength properties of the material.

Table 4.6: Summary of the improvement in mechanical properties for ACNT ASGFRP composite (amine-rich resin system)

S. No.	Mechanical Properties	EP GFRP composite	ACNT ASGFRP composite (amine-rich resin system)
1.	Tensile Modulus (GPa)	6.4	7.4 (+15%)
2.	Tensile Strength (MPa)	268	289 (+8%)
3.	Flexural Modulus (GPa)	7.3	9.1 (+26%)
4.	Flexural Strength (MPa)	131	260 (+97%)
5.	ILSS (MPa)	1.81	3.35 (+ 85%)

On the other hand, the improvement in the tensile strength of ACNT based composites may be attributed to two reasons: firstly due to better dispersion of the amino functionalized nanotubes in amine-rich resin epoxy matrix composition, likely due to weak van der Waals forces and use of homogenization and sonication processing techniques. Secondly, the excess amino groups in the matrix bonded with the resin at multiple sites that allowed the transferring of load from the matrix to the outer layer of amino-CNTs during longitudinal testing mode [Zhu *et al.*, 2004].

Figure 4.10 demonstrates the stress-strain relationship for ACNT ASGFRP composites prepared in amine-rich resin system (69%), using optimal conditions, and compares it with different ACNT GFRP composites manufactured.

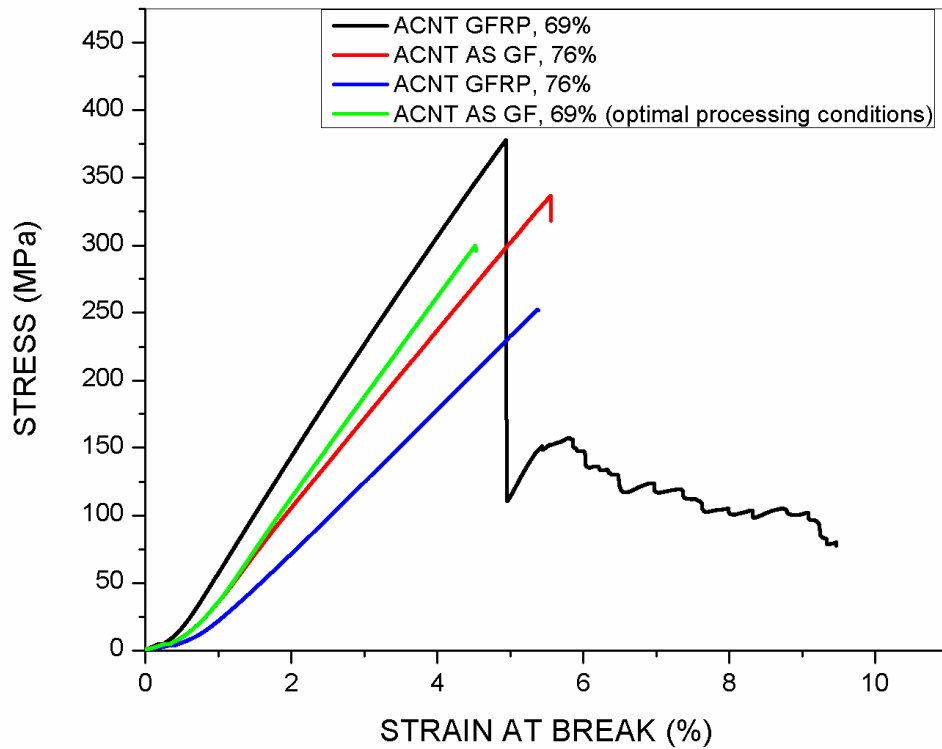


Figure 4.10: Behavior of stress as a function of strain for ACNT ASGFRP composites (69%, optimal processing conditions) as compared to other ACNT GFRP composites

Few of the key observations from the graph are: (i) ACNT GFRP composites prepared at the stoichiometric ratio (76%), shows significant drop in strength and modulus while, strain at break increases as compared to composites with amine-rich resin composition, ACNT GFRP (69%); (ii) Further, modifying the glass fibres with amino silane (ASGF) while keeping the matrix composition unchanged i.e. ACNT GFRP (76%), shows higher stiffness, strength, and ductility. However, if a composite is prepared with optimal matrix and fibre treatment, i.e. ACNT epoxy matrix with ASGF in amine-rich resin, it lowers its strength and strain values while its stiffness increases as compared to similar composite prepared at stoichiometric ratio. Therefore, it can be stated that the silane treatment of glass fibre transformed the ductile behavior of ACNT composite to brittle behavior.

In conclusion, this study has been able to successfully identify and optimize the conditions required for reinforcing EP GFRP composites with both functionalized and non-functionalized nanotubes. In addition, the effect of surface treatment of glass fibres on the fibre-matrix interface has also been thoroughly explored and the major findings have been

documented. In order to implement these composites for marine structural components it is essential to explore their overall performance when subjected to seawater. The excellent properties of CNT GFRP composites would be beneficial for commercial/industrial applications only if they reveal minimum degradation and damages even after exposure to varying hygrothermal conditions and durations and the same has been discussed in the next chapter.

4.4 Closing remarks

The fibre - matrix interface was found to be strengthened by treating the glass fibre surface with epoxy and amino silane coupling agents. The mechanical performance of ACNT reinforced composites increased in the case of AS treated glass fibre. This was possibly due to the formation of 3-D cross linked network and CNT-bridging mechanism observed between ACNT and AS glass fibre through the epoxy matrix attached to glass fibres. On the other hand, PCNT composites showed appreciable improvement in mechanical properties when fabricated with ES fibres. This could be due to the bonding of ES with glass fibres and epoxy hardener. The surface treatment of glass fibres transformed the fracture mode of composites from ductile to brittle. Lastly, dispersion of amino-CNTs in hardener has shown considerable improvement in mechanical properties as compared to EP GFRP and ACNT GFRP specimens. Simultaneously, FTIR and SEM characterization techniques have verified the crosslinking reactions and the presence of enhanced fibre-matrix interface.

Chapter 5. Hygrothermal aging of composites

5.1 Introduction

Until now the focus of the study was to improve the performance of EP GFRP composites for preparing marine structures either by incorporating nanotubes or surface treatment of glass fibres or a combination of both. The structural GFRP components used in ships, boats etc. consist of glass fibre strongly bonded through a thermosetting matrix, mainly epoxy resin because of its excellent properties such as low shrinkage after curing, good resistance to corrosion and stability at higher temperatures. Although, the use of GFRP composites for naval or underwater applications is increasing rapidly still it is a challenging task. A particular challenge faced in the marine environment by the FRP composites is that on exposure to sea water and/or moisture conditions, it causes plasticization effect. Due to which, it initiates material degradation and weakens the fibre-matrix interface. Considering these issues, the focus of the present study was to improve the design of existing GFRPs by incorporating CNTs, or silane treatment of GFs. The objective was to expose the fabricated advanced/multifunctional GFRP composites to hygrothermal environment and evaluate their performance. The different parameters that play a key role during the hygrothermal study of GFRP composites and hence affect the different properties are listed in Table 5.1 and explained ahead in detail.

Table 5.1: Key parameters of hygrothermal study

S. No.	Key parameters	Properties that are affected
1.	Type of water	Diffusion of water Mechanical properties Morphology Interfacial adhesion
2.	Temperature of water	
3.	Sample composition	

During hygrothermal conditions the type of water significantly affects the water uptake content, interfacial adhesion, mechanical properties and the type of damage caused. It happens due to the variation in the sorption mechanism observed for different water concentrations and their reactivity. In order to understand the diffusion mechanism, researchers have experimented hygrothermal aging of GFRP in sea water, distilled water, de-mineralized water etc. It was generally observed that the absorbed equilibrium moisture content for GFRPs was higher in distilled/de-mineralized water than in seawater [Chifu and Iroh 1996, Davies *et al.*, 2001, Wu *et al.*, 2002, Barraza *et al.*, 2003, Kootsookos and Mouritz 2004, Mula *et al.*, 2006, Surathi and Karbhari 2006, Kar *et al.*, 2008, Aldajah *et al.*, 2009]. This has been attributed to the formation of the salt layer on the immersed surfaces which reduces the diffusion of water molecules significantly. Additionally, another important finding revealed that during the initial stages of absorption, the water uptake follows Fick's Law [Carter and Kibler 1978, Popineau *et al.*, 2005] but on prolonged aging it no longer follows Fickian behavior. Firstly, the diffusion process of water into the composites is also dependent upon the concentration gradient of water molecules outside and inside the polymer and is quantitatively measured as Diffusion coefficient (D). The calculation of D values has been discussed in detail in Section 5.3.1. Secondly, the exposure temperature of the water also significantly affects different properties, listed in Table 5.1. From the literature, it is interpreted that the water absorbed by the matrix at room temperature (20 – 25°C) acts as a plasticizer, tends to lower the glass transition temperature (T_g) and causes swelling of the matrix. In general, the effect of water absorption on the mechanical properties at room temperature is less serious as compared to higher temperatures. Recently, a study by Netravali [Netravali *et al.*, 1985] compared the T_g , weight gain and curing energy of aged and dry specimens and revealed that the effect of water absorption in epoxy matrix on T_g and water uptake content at room temperature was a reversible process. While, at elevated temperatures there was a chemical reaction between the water and the unreacted epoxide groups, which caused a permanent change in the physical and chemical nature of epoxy. Furthermore, aging at higher temperature resulted in increasing the water content in the composite, induced swelling of the matrix that led to faster occurrences of damages such as crack formation, stress concentration sites, fibre-matrix debonding etc. thus affecting the stability and behavior of the composite. Recently [Karbhari and Zhang 2003] the durability of 2 and 4 layered specimens of E-glass/Vinylester composition on immersion in deionized water was investigated at two different

temperatures and potassium based pH. From the study, it was concluded that the moisture uptake content and diffusion coefficient was maximum for samples immersed in DW at higher temperature and also results in a significant drop in tensile modulus and strength properties.

From the above discussion, it is clear that the ingress of water into the composite forms the basis of material degradation. In the case of EP GFRP composites, it has been observed that initially the water enters through the matrix and after prolonged aging enters the fibres or fibre-matrix interface. Hence, as the aging time increases the water molecules interact with the fibres and influence the mechanical properties of the composite, such as strength, rigidity, and strain at failure. Additionally, the changes in thermal, physical, and chemical properties of either epoxy matrix or glass fibre eventually affect the mechanical properties of composites and induces damage. The damage might initiate within the matrix, within the fibre, or at the fibre-matrix interface region but it depends upon the damage mechanism. The failure under such conditions could be either cohesive (failure within the matrix) or adhesive (interfacial) failure or even fibre failure may occur.

Another important factor that affects the durability of composites on exposure to water is its composition, as listed in Table 5.1. The composition refers to its basic constituents such as type of polymer matrix, fibres and nano-fillers if any. Extensive research carried out on GFRP composites exhibited deteriorating behavior. It was then that researchers attempted to improve the behavior of GFRP materials in moist conditions by incorporating various nano-fillers in GFRPs, following *in-situ* polymerization, such as carbon nanotubes (CNTs), nanoclay and carbon nanofibers. Among these nano-fillers, CNTs possess superior properties in various disciplines and are thus, incorporated for various industrial applications [Yu M-F *et al.*, 2000, Zhang *et al.*, 2009, Burkholder *et al.*, 2011]. Although, CNT GFRP (hybrid) composites have attracted substantial attention in various commercial applications, but not much research has been carried out to investigate the effect of moisture/water absorption on the material degradation of CNTs-reinforced composites [Zulfi *et al.*, 2013, Barkoula *et al.*, 2009, Prolongo *et al.*, 2012, Zafar *et al.*, 2012, Starkova *et al.* 2013]. It was recently, in last five years, that scientists were forced to shift their focus on exploring the behavior of CNT reinforced polymer composites under hygrothermal conditions. The investigation led by Prolongo [Prolongo *et al.*, 2012] and Zafar [Zafar *et al.*, 2012] analyzed the effect of water and/or moisture uptake in hybrid

composites and reported a significant effect on the diffusivity coefficient, mechanical properties and T_g . It was also mentioned that such behavior was probably due to higher barrier properties of CNTs pertaining to their high-specific area: $300 \text{ m}^2/\text{g}$ and strong chemical bonding between the nanotubes and the epoxy resin. However, studies related to the effect of seawater on the absorbed water content, rate of diffusion and mechanical properties of the hybrid composites are minimal.

In view of the above discussion, the objective of this chapter is to evaluate the performance of fabricated GFRP composites after long-term aging in a hygrothermal environment. Samples with different matrix compositions such as EP GFRP, ACNT GFRP, PCNT GFRP as well as surface treated fibres with either amino or epoxy silane in neat epoxy compositions were examined after aging in simulated seawater and distilled water. The water uptake content, diffusivity coefficient and material degradation were correlated by considering the chemical interaction of water with the matrix and morphology of submerged samples. In addition to the above mentioned factors, effect of epoxy-edge coating with respect to its mechanical properties has been investigated for different GFRP compositions. The present study focused on comparing material degradation and durability of various GFRP composites when exposed to high (55°C) as well as low (25°C) temperature seawater conditions. It is known from the literature that a 10°C rise in temperature causes a doubling of diffusion rate, so this would correspond to an eight times acceleration in diffusion at 55°C as compared to 25°C aging. These observations are presented and discussed ahead in this chapter.

5.2 Experimental set-up

Since, the composition of real seawater is not constant, water of the identical composition as per ASTM D1141-98 was prepared in the laboratory. The major salt components dissolved in the sea water as per ASTM standard are presented in Table 5.2. The pH was maintained in the range of 7.9 to 8.1 throughout the experimental study.

For hygrothermal aging of the specimens, a water bath with temperature control having an accuracy of $\pm 0.1^\circ\text{C}$ was used. In order to assess the water uptake by the EP GFRP and hybrid composites, the specimens were immersed into SW and DW at 25°C as shown in Figure 5.1. The water level has been depicted by highlighting in red and marked by arrows in yellow as represented in Figure 5.1.



Figure 5.1: Hygrothermal aging of EP GFRP and CNT GFRP samples on immersion in water bath when studied in a seawater environment

Table 5.2: Concentration of salts in simulated seawater

S. No.	Element	Concentration, (g/L)	Weight %
1.	NaCl	24.530	68.100
2.	MgCl ₂	5.200	14.400
3.	Na ₂ SO ₄	4.090	11.400

4.	CaCl ₂	1.160	3.220
5.	KCl	0.695	1.930
6.	NaHCO ₃	0.201	0.558
7.	KBr	0.101	0.280
8.	H ₃ BO ₃	0.027	0.0749
9.	SrCl ₂	0.025	0.0694
10.	NaF	0.003	0.00833

5.3 Methodology

A quantitative analysis has been carried out for the conditioned samples by evaluating their behavior as compared to the unconditioned sample. Firstly, the kinetics of water absorption mechanism was analyzed to determine the equilibrium mass water uptake content (M_x), mass water uptake (M), and the diffusion coefficients (D). Secondly, the change in mechanical properties over increasing immersion time for different sample compositions was also done. Additionally, the fracture test samples were analyzed under SEM along with EDS analysis to examine the morphology of the fracture surfaces, different failure mechanisms and to find out the extent of salt intake by the composites.

Lastly, few conditioned samples were analyzed for chemical changes in the interface using FTIR. The above study related to aging has primarily been carried out at 25°C and has been extended to observe the effect of increase in water temperature up to 55°C. This elevated temperature lies below the curing temperature (70°C) and T_g of the cured EP GFRP composite which is 69°C, as determined by DSC analysis.

5.3.1 Calculating water uptake content and diffusivity rate

The edges of test specimens (prepared according to ASTM D790) were coated with a thin layer of epoxy resin prior to their immersion in water bath as shown in Figure 5.1. The edges of the samples are sealed with a thin layer of epoxy coating so that the moisture enters

predominantly through the surface of the specimen. The coating lowers the moisture absorption content and plasticization effect and thus illustrates better shear strength as compared to uncoated specimens [Adams and Singh 1995, Wimolkatisak and Bell 2004]. In order to study the relation between exposure time and its immediate effect on the mechanical properties, the samples were immersed for 15, 30 and 90 days in both SW and DW. After the specific time intervals, the test specimens were removed from the water bath, wiped with cloth, left in the air to dry (6-7 min) and then weighed on a balance with a least count of 0.1 mg. On the other hand, for the study related to kinetics of water absorption, another set of EP GFRP and hybrid specimens were submerged in SW and DW for a maximum period of 121 days. These specimens were removed from the water bath after 1-day intervals of conditioning time, wiped with cloth, left for air drying (6-7 min) and then weighed. The water uptake, M , was calculated and expressed as a percentage of the initial weight of the specimen according to the Equation (5.1).

$$M = \frac{W_w - W_D}{W_D} \quad (5.1)$$

where, M , W_w and W_D are the weight gain of the composites, the weight of the wet sample and weight of the dry sample, respectively.

After successfully plotting and analyzing the percent weight gain of the composites versus the square root time graph, area with no significant change in weight gain with respect to time was considered as the saturation water content and reported as mass at equilibrium (M_x). The weight gain by the composites is dependent on the rate of diffusion of water and is expressed in terms of the diffusivity coefficient (D) which was calculated by using Equation (5.2):

$$D = \frac{\frac{M_t^2}{M_x} \times \pi \times h^2}{16 \times t} \quad (5.2)$$

where, M_t refers to water content at time 't', h is thickness of the specimen, and t is the immersion time.

5.3.2 Hygrothermal conditions

As outlined and discussed above, several parameters seem to play a major role in the hygrothermal behavior of EP GFRP and CNT GFRP composites. Thus, in the present study different types of GFRP composites under various hygrothermal conditions were investigated and the details of the same have been mentioned in Table 5.3 and discussed ahead. A temperature of 25°C was chosen for the present investigation as it closely reflects the actual seawater temperature.

Table 5.3: Types of samples tested for different hygrothermal aging conditions

S. No.	Type of composite	Hygrothermal conditions
1	EP GFRP	• Seawater at 25°C • Distilled water at 25°C • Seawater at 55°C
2	EP ASGFRP	• Seawater at 25°C • Seawater at 55°C
3	EP ESGFRP	• Seawater at 25°C • Seawater at 55°C
4	ACNT GFRP	• Seawater at 25°C • Distilled water at 25°C • Seawater at 55°C
5	PCNT GFRP	• Seawater at 25°C • Distilled water at 25°C • Seawater at 55°C

5.3.3 Characterization

Flexural tests were carried out according to ASTM D790 on Zwick Roell Z10 machine. The strength, modulus, and ILSS were evaluated using 3-point bending mode at a crosshead speed of 1.34 mm/min. For flexural tests, the span-to-width ratio was kept at 25.4 mm as per ASTM standard, since the thickness of the specimens was less than 1.6 mm. Four samples were

tested for each of the composite prepared ILSS has been calculated following the ASTM D-2344.

The water diffused in GFRPs tends to interact with epoxy-amine network and reduces its mechanical properties. The chemical interaction between the water molecules and the polymer matrix has been carried out using FTIR (Perkin-Elmer FTIR spectrometer) spectroscopy. The samples of the unconditioned and conditioned (15, 30 and 90 days) EP GFRP composites were analyzed. In order to prepare the samples for FTIR image, a 1×1 cm specimen was cut from the respective conditioned flexural laminates and pressed into a pellet with KBr and scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

SEM was performed with JEOL JSM 6510LV SEM operated at 20kV. Prior to the SEM analysis, all specimens were sputter-coated with a thin layer of gold to avoid charging effects. EDS was also recorded for the conditioned specimens after their morphological characterization to determine the concentration of different salts present in the composite specimens.

5.4 Results and discussion

In this section the order of results discussed is as follows:

1. Diffusion studies of: EP GFRP, ACNT GFRP and PCNT GFRP samples when immersed in SW and DW at 25°C
2. Mechanical analysis along with morphology of the above mentioned samples
3. Effect of edge coating of specimens on the diffusion of water and the resulting mechanical properties
4. Degradation at elevated temperature for: ACNT GFRP, PCNT GFRP, silane treated EP GFRP samples in reference to water uptake content, flexural modulus and strength.

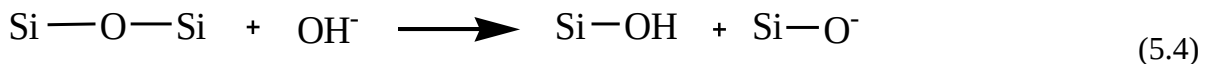
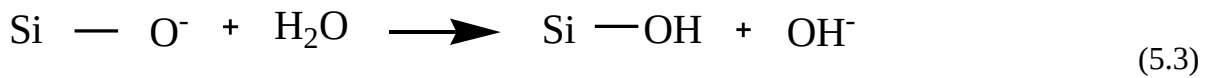
5.4.1 Diffusion studies

5.4.1.1 CNT modified GFRP composites at room temperature

Figures 5.2 and 5.3 demonstrate the water infusion behavior along with % weight gain versus time for both EP GFRP and CNT GFRP (hybrid) composites on conditioning in SW and DW, respectively. In general, the diffusion curves for EP GFRP specimens in SW and DW show a similar behavior over the aging time. During the first 432h or 18 days aging, the EP GFRP

specimens demonstrated an increasing trend (except for one outlier data point), thus suggesting Fickian behavior and also attained the maximum water content level for that time. Several studies on GFRP composites have already confirmed that the Fickian behavior usually fits the data points during the initial stages of the sorption, but fail to describe the same as aging time increases [Frisch 1968, Aditya and Sinha 1992, Roy *et al.*, 2000, Ellyin and Rohrbacher 2000, Jiang *et al.*, 2012, 13]. A similar behavior for polymer matrix composites has also been reported by other researchers [Adams and Singh 1995, Ellyin and Rohrbacher 2000, Iglesias *et al.*, 2002, Tsenoglou *et al.*, 2006, Kar *et al.*, 2008, Mourad *et al.*, 2010, Abhilash *et al.*, 2011, Prolongo *et al.*, 2012, Zafar *et al.*, 2012, Zulfi *et al.*, 2013]. On the exposure of GFRP composites to moist or water environment, the exposed surface instantly absorbs water by capillary action, followed by diffusion through the matrix. The absorbed water from the surface diffuses into the polymer matrix and occupies the free volume of the material. The amount of free volume actually depends on the extent of resin curing and the cross-linking density of the composite. Another possibility of excess water uptake during initial stages is due to the presence of hydroxyl groups in epoxy resin which tends to absorb water molecules.

Interestingly, after 432h (18 days) the water absorption did not continue to follow the same trend, i.e., water content started to decrease for several days. The sorption behavior for EP GFRP and CNT GFRP specimens as shown in Figure 2 has been observed for the first time. There are possibly several reasons which account for the immediate drop in water content after reaching the maximum level. Firstly, it might be due to the development of cracks, delamination, debonding, etc., inside the composites due to the excess water uptake that caused swelling of the epoxy matrix. Another possible reason could be the chemical interaction of glass fibres with the surrounding water molecules as defined by the reaction mechanisms shown in Equations (5.3) and (5.4).



The reaction mechanism reveals the presence of Si-OH and SiO₂ elements in the composites that possibly leached out from the glass fibre surface into the water during their

conditioning, thus causing a decrease in weight of the samples. Lastly, studies have reported that such behavior could also be a result of stress relaxation which occurs due to swelling after water absorption [Berens and Hopfenberg 1978, Pritchard and Speake 1987, Pereira *et al.*, 2016]. Overall, the water absorption behavior reported in the present study shows a different trend which has not previously been reported in the literature for GFRP composites. Thus, it can be stated that although the trend observed is different from the literature, but the fundamental aspects are somehow same. Also, it is difficult to explain such complex mechanism with a single theory or model since it varies with the type of polymer matrix chosen, curing conditions and the extent of cross-linking density of the material.

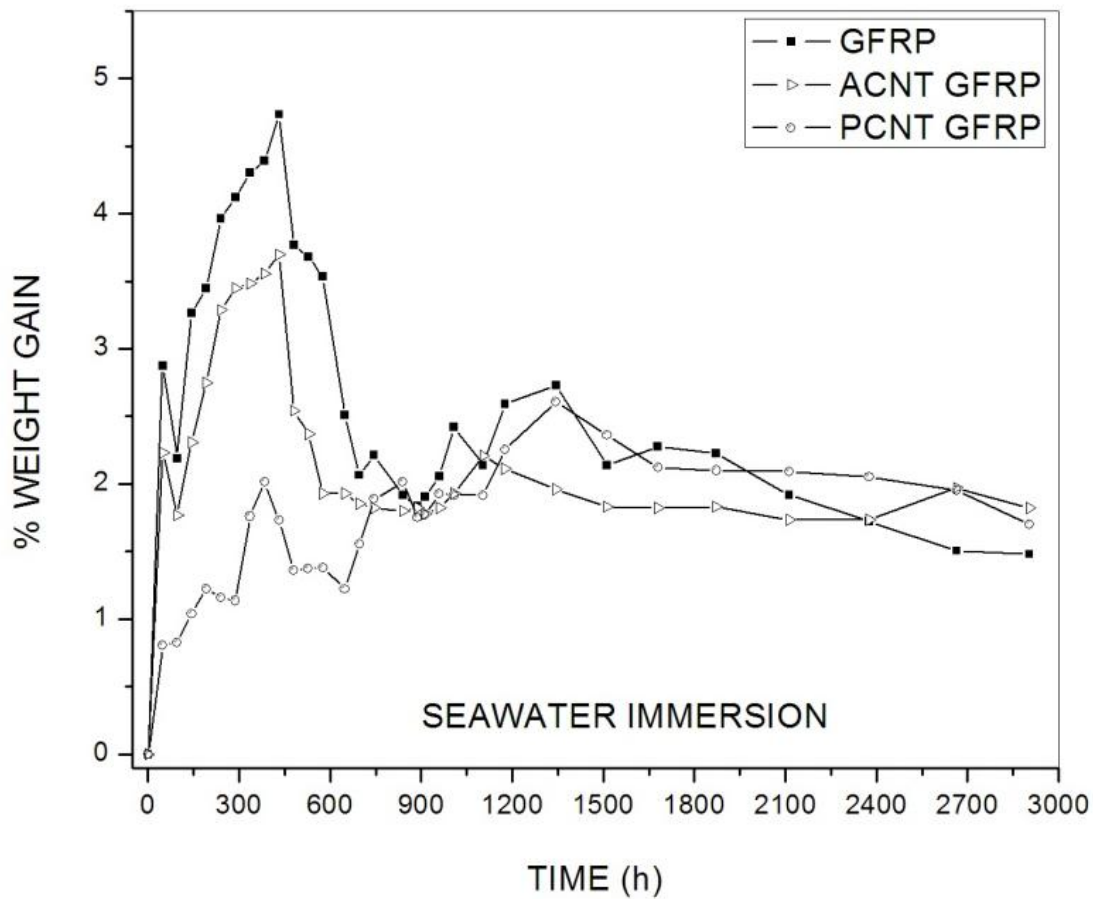


Figure 5.2: Water uptake behavior of EP GFRP and CNT GFRP composites on exposure to seawater at 25°C

From Figures 5.2 and 5.3, it can also be noted that for EP GFRP specimens, the maximum water content (M_{∞}) of 4.85% and 5.05% was attained after 432 h (18 days) and 336 h

(14 days) of immersion in SW and DW, respectively. Along with % weight gain, diffusion coefficient (D) was also calculated by using Fick's Law up to the aging time for which the maximum water intake occurred. Table 5.4 lists the experimentally determined D and M_x values for the composites studied. The D values of 3.885×10^{-7} and 2.257×10^{-7} mm²/sec were calculated for EP GFRP composites on immersion in SW and DW (rows 1a and b in Table 5.4), respectively. Also, analogous to % weight gain, the diffusion rate is higher for DW vis-à-vis SW immersion.

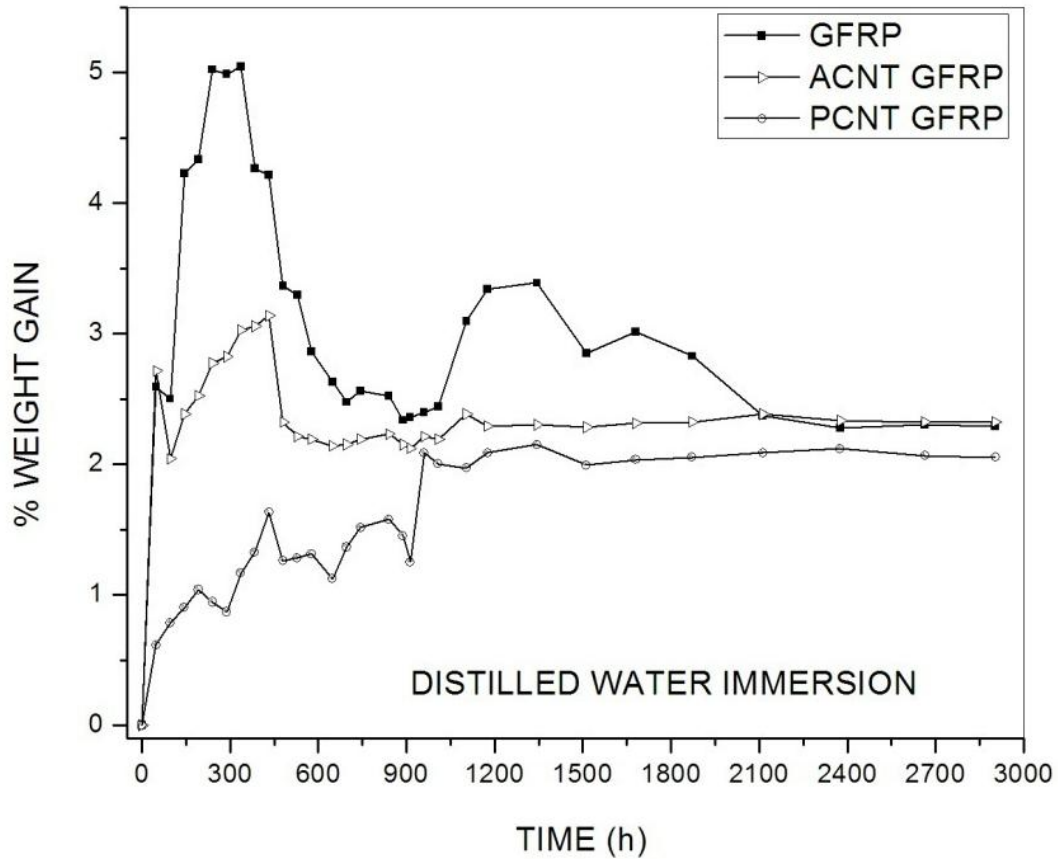


Figure 5.3: Water uptake behavior of EP GFRP and CNT GFRP composites on exposure to distilled water at 25°C

The possible explanation of such behavior is that (i) the salt particles and/or trace elements in SW were less readily absorbed into the matrix; (ii) the bulky nature of salt water molecules in SW inhibited the water absorption; and (iii) the scale formation on the surface of specimens restricted the capillary motion of water into the composites and lastly, the salt

concentration outside the composite was higher as compared to inside the specimen, thus creating an osmotic pressure that again acted against the water absorption [Yang *et al.*, 2008b, Barkoula *et al.*, 2009, Prolongo *et al.*, 2012, Zafar *et al.*, 2012]. Similar diffusivity behavior and increased rate of water absorption in distilled/deionized water over seawater have been witnessed by other researchers as well [Lagrange *et al.*, 1991, Adams and Singh 1995, Ahmad *et al.*, 2011, Zafar *et al.*, 2012, Rao *et al.*, 2014, Bortolin *et al.*, 2012].

On the other hand, it was analyzed from Figures 5.2 and 5.3 that the incorporation of CNTs in epoxy matrix significantly reduced the maximum water uptake content as compared to EP GFRP specimens. ACNT GFRP samples show maximum water content of 3.69% and 3.14% after 432 h (18 days) immersion in SW and DW, respectively. Whereas, PCNT GFRP composites show a maximum water content of 2.61% and 2.15% after 55 days of conditioning in SW and DW, respectively. As expected, the diffusivity rate into hybrid composites was also affected. For ACNT GFRP specimens, the diffusion rates were found to be $3.287 \times 10^{-7} \text{ mm}^2/\text{sec}$ in SW and $1.526 \times 10^{-7} \text{ mm}^2/\text{sec}$ in DW (refer to rows 2a and b in Table 5.4). And, for PCNT GFRP specimens, the diffusion rates were 4.068×10^{-8} and 3.082×10^{-8} on aging in SW and DW, respectively. Quantitatively, there was approximately 15% and 32% drop in D values for ACNT samples immersed in SW and DW, respectively as compared to hygrothermally aged EP GFRP specimens. A similar fall in wt% and D values has recently been reported by Prolongo [Prolongo *et al.*, 2012] for ACNT composites. In addition to this, it was also concluded that D values plunge even further by increasing the CNT concentration in the composites. Also, their experimental study revealed that even though these CNT composites absorbed lower moisture content, but their plasticization effect was much greater. The lower weight gain ($M\%$) and diffusion rate in hybrid composites are likely due to two main reasons: Firstly, the barrier properties of CNTs in epoxy matrix formed a tortuous path, thus slowing the sorption of water into the composite interface. Secondly, the presence of strong covalent bonds between the amino-functionalized CNTs and the epoxy matrix also attempted to delay the movement of water molecules through the composite. Lastly, the nano-fillers dispersed in the matrix occupy the free volume spaces and thus reveal a significant effect on the amount and distribution of the free volume [Starkova *et al.*, 2013].

In all the nanocomposites (ACNT and PCNT) specimens, irrespective of the water in which they are conditioned, the water uptake content was found to be lesser than the neat epoxy. Where PCNT being hydrophobic in nature and uniformly dispersed in resin reduced the free volume of the material and consequently resulted in minimum water absorption.

Table 5.4: Equilibrium water content and diffusion coefficients for different GFRP composites and hygrothermal conditioning

S.No.	Specimen	Conditioning	Diffusion Coefficient, (D) , (mm^2/s)	Equilibrium water content, M_x , (%)
1a	EP GFRP	Sea water at 25°C	3.885×10^{-7}	2.21 after 63 days
1b	EP GFRP	Distilled water at 25°C	2.257×10^{-7}	2.56 after 63 days
2a	ACNT GFRP	Sea water at 25°C	3.327×10^{-7}	1.82 after 63 days
2b	ACNT GFRP	Distilled water at 25°C	1.654×10^{-7}	2.19 after 63 days
3a	PCNT GFRP	Sea water at 25°C	4.802×10^{-8}	1.89 after 72 days
3b	PCNT GFRP	Distilled water at 25°C	2.864×10^{-8}	2.06 after 63 days

From the above diffusion study, it can be stated that by controlling the ingress of water into the composite interface following benefits could be achieved: slower diffusion of water, lesser degradation of the material, ability to sustain the hygrothermal environment for a longer time thus enhance the durability of the composite, incur lower maintenance costs and higher

service life. A material fulfilling all these requirements would certainly benefit the naval industry at large. Hence, to quantitatively support this, the mechanical behavior of conditioned specimens needs to be evaluated and compared with unconditioned specimens.

5.4.2 Performance evaluation

This section discusses about the effects of hygrothermal aging on the mechanical properties of EP GFRP and CNT GFRP composites versus aging time. The average of the flexural properties of the specimens after immersion in water for 15, 30, 90 and 121 days has been compared to the unaged (reference/control) specimen.

5.4.2.1 EP GFRP composites

Figure 5.4 shows the effect of aging of EP GFRP specimens immersed in SW and DW on the flexural modulus, strength, ILSS, and elongation at break properties. It can be seen that when immersed in SW, the flexural modulus value drops for EP GFRP specimen's, from 7.3 GPa to 5.8 GPa, within 15 days of aging as compared to unaged sample. Interestingly, after the initial drop (360h/ 15 days), the laminate regains its stiffness, to 6.3 GPa, at mid-time (720h/ 30 days) and reaches to 6.7 GPa at the end of 121 days aging. EP GFRP specimens conditioned in DW also showed a similar trend, with the exception that the percent regain in stiffness (after 15 days) was 19% higher than observed for SW aged samples (refer to flexural modulus in Figure 5.4). Also, at the end of 121 days i.e. 2904h aging period, the composite had a modulus of 7.4 GPa which was higher than the control specimen.

This behavior observed for flexural modulus of EP GFRP samples immersed in SW and DW is because the epoxy resin interacts differently with water during the initial stages. At the beginning, the absorbed water interacts chemically with the epoxy matrix through van der Waals forces and hydrogen bonds, acts as a plasticizer, and results in increased chain segment mobility (Type I water). Consequently, it lowers the glass transition temperature, mechanical strength, and elasticity of the materials [Prolongo *et al.*, 2012].

Further, the non-homogenous water absorption introduced localized defects, such as fibre pullouts as shown in Figure 5.5(a), which acted as stress-concentration sites during flexural loading [Mourad *et al.*, 2010, Chakraverty *et al.*, 2015].

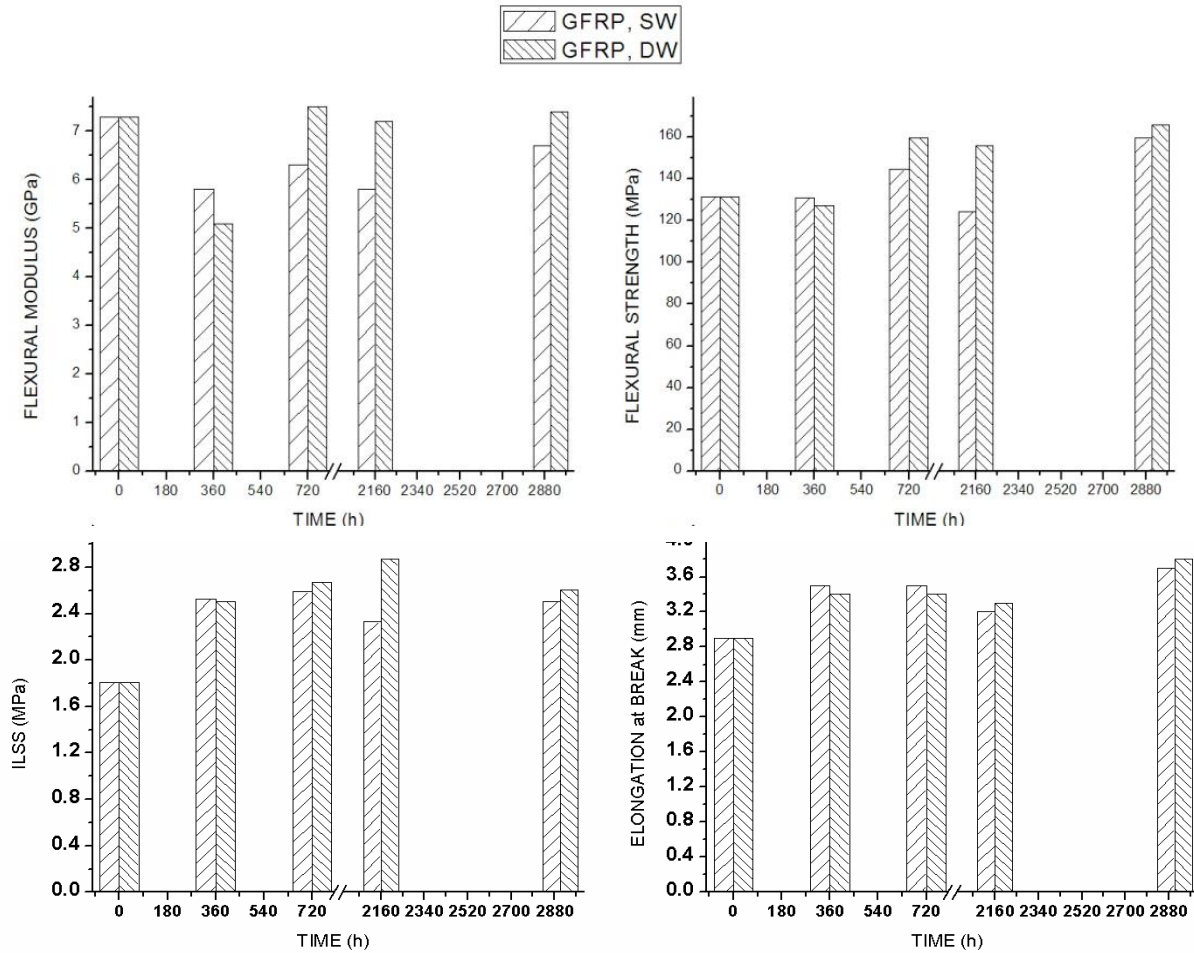
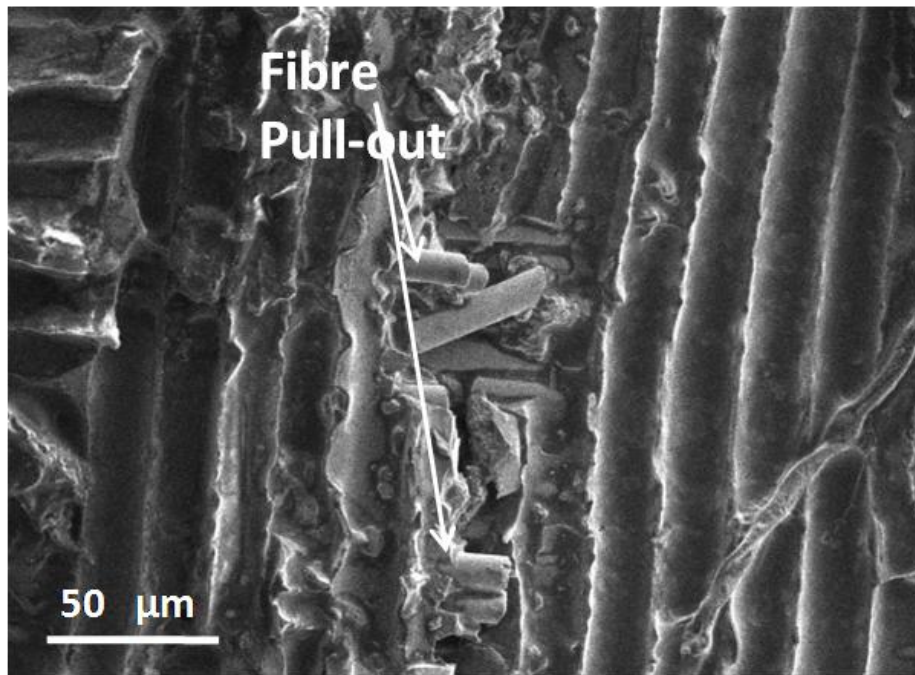


Figure 5.4: Effect on flexural properties of EP GFRP specimens after immersion in SW and DW for increasing aging time

Interestingly, there was considerably more reduction for samples immersed in DW as compared to SW because of higher moisture content in fibre-matrix interface that degraded the interface, visualized as fibre pullouts and cusp formation as shown in Figure 5.5(b) [Rao *et al.*, 2014]. On the other hand, the recovery in modulus values is attributed to the swelling of the matrix, caused due to excess water uptake inside the fibre-matrix interface that eventually improved the mechanical adhesion between them.

Hence, the reversing trend results in decrease of modulus only by 8% after 121 days aging in SW.

(a)



(b)

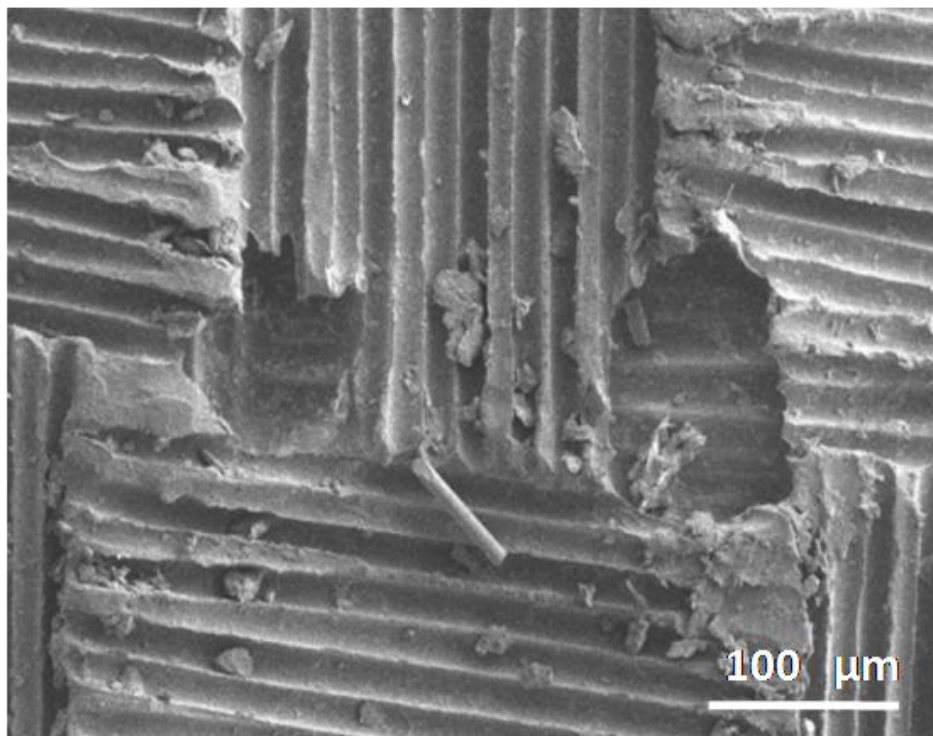
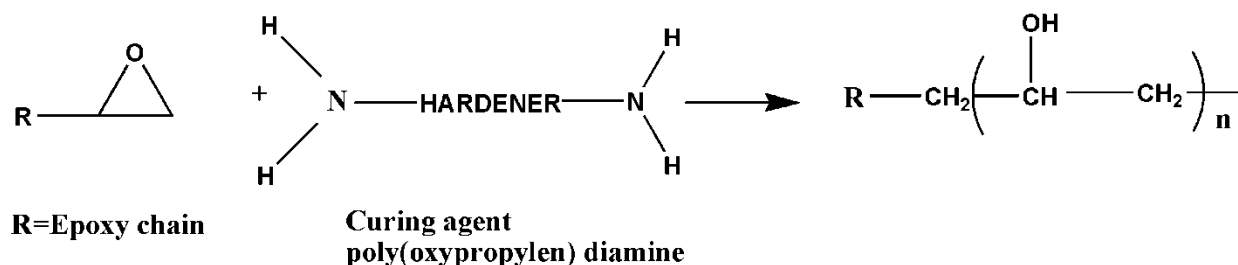


Figure 5.5: Damage on fibre-matrix interface after 360h (15 days) of immersion in (a) SW and (b) DW

On the contrary, other properties such as flexural strength, ILSS, and elongation at break in general showed an increasing trend versus immersion time. Specifically, in the case of flexural strength, maximum enhancement was recorded to be 21% for SW and 26% for DW after 121 days of aging as compared to the unaged sample, with strength of 131 MPa. The increase in strength of the composites may be due to the relaxation of residual stress inside the fibre-matrix interface. Another possible reason may be that due to the enhanced diffusion of SW into the composite, the concentration of Na^+ ions increases considerably and undergoes a chemical reaction with the hydroxyl groups of cured epoxy and the glass fibre surface as shown in Figure 5.6. As a result, it enhanced the process of bond formation and showed improvement in strength/stiffness of the composite material.

Reaction 1: DGEBA epoxy and diamine hardener



Reaction 2: Epoxide chain with excess sodium ions freely available in the water

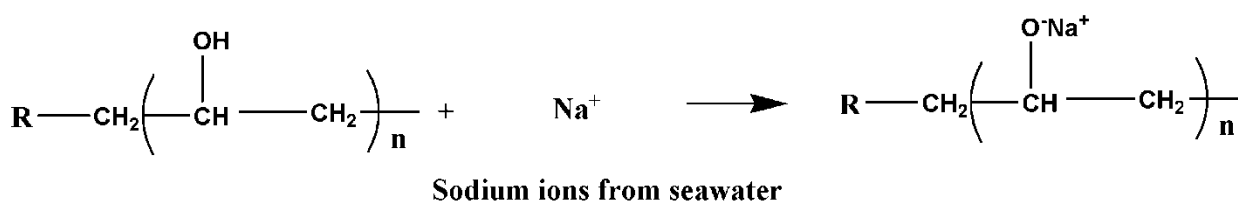


Figure 5.6: Reaction mechanism between cured epoxy resin and sodium ions from SW

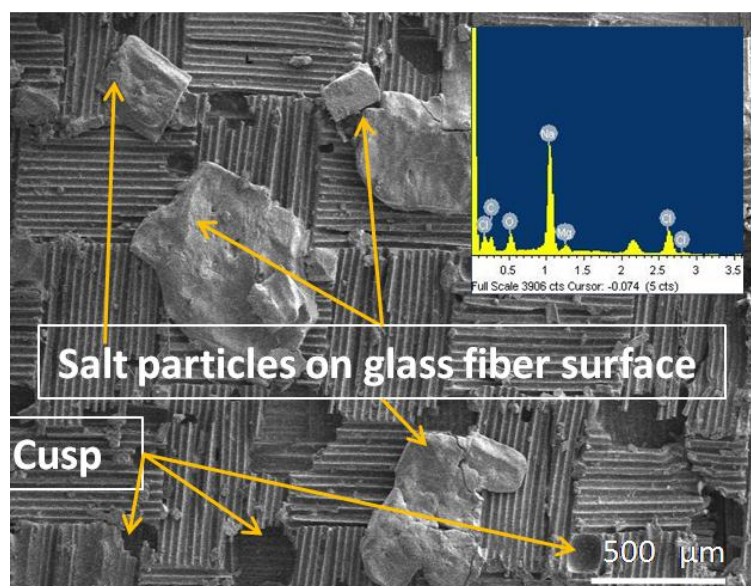
Furthermore, it is known that plasticization of the matrix results into lower modulus, but higher strain at break. The same was also observed from the experimental results of this study. Also, on prolonged aging, 2160h (90 days), seawater molecules were visible on the fibre surface as shown in Figure 5.7a, which altered the mode of failure from a brittle matrix and ductile fibre to ductile matrix and brittle fibre [Chakraverty *et al.*, 2015]. The inset (in Figure 5.7a) illustrates the EDS spectra of the seawater molecules which highlight its composition i.e. Na^+ and Cl^- ions

thus confirming the diffusion of seawater from the surroundings into the composites interface. Similarly, the ILSS properties for SW-conditioned samples continued to show an improvement with aging time, reaching a maximum (2.59 MPa) after mid-time and almost stabilized after that. The increase may be due to mechanical interlocking at the fibre-matrix interface, deposition of large salt particles, thus forming a resin-rich layer on the glass fibre surface (as shown in Figure 5.7a), which resisted the shear deformation during the application of external load [Kar *et al.*, 2008].

On the other hand, for DW immersion, EP GFRP samples exhibited a minimal fall in strain at break as compared to samples of the same composition immersed in SW. Also, the material shear strength improved thus reaching a maximum value of 2.87 MPa and revealed an improvement of 7.5% after 90 days exposure as compared to the sample aged for 30 days. SEM images of fractured sample support these results.

In Figure 5.7b, it is clearly seen that the fibres are broken and the surface is more rough as compared to that in Figure 5.7a. The broken fibres reveal the materials brittle failure, which possibly affected the ductility of the composite. In addition to that, the rough surface indicates the presence of a strong bond between the matrix and the fibres, which as a result improved the shear strength of the EP GFRP composite. It is important to state that in these specimens, the bulky salt water molecules were missing inside the composite interface for all aging times.

(a)



(b)

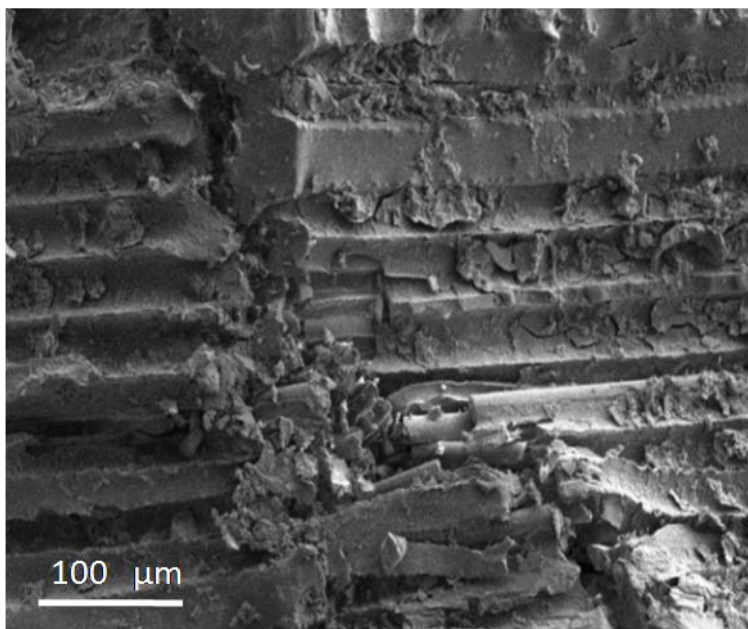


Figure 5.7: SEM image illustrating the morphology of EP GFRP specimens after 90 days exposure in (a) SW and (b) DW

On the whole, it was observed that as the water content inside the fibre-matrix interface decreased, the mechanical properties recovered. Thus, confirming the initial hypothesis that at room temperature (25°C) the effects of aging are a reversible process. Also, the effect of seawater was more profound than the distilled water.

5.4.2.1.1 FTIR analysis of the aging process

Water absorbed into the composite undergoes a chemical interaction between water molecules and the epoxy-amine network. FTIR spectroscopy is used primarily for qualitative and quantitative analysis of organic compounds. But in this study, FTIR spectrum attempts to quantify the amount of water absorbed into the polymer matrix composites versus immersion time by analyzing the intensity of FTIR peaks at specified wavelengths.

In general, water is believed to have two active vibration modes which correspond to the stretching (within $3900 - 2800 \text{ cm}^{-1}$) and in-plane bending (within $1650 - 1590 \text{ cm}^{-1}$) of O-H. Previous studies have reported that water exists in two forms when absorbed by the epoxy matrix, i.e., highly mobile-free water molecules (around 3600 cm^{-1}) and water molecules

attached to the epoxy network through hydrogen bonding (around 3300 cm^{-1}) [Cotugno *et al.*, 2005, Blanco *et al.*, 2006]. The FTIR spectra of conditioned EP GFRP composites with varying immersion times, i.e., 15, 30 and 90 days have been compared with the unaged specimen as shown in Figure 5.8. The graph is in transmittance mode, which signifies that absorbance is less. Also, the value of the intensity of the peak indicates the degree of cure of resin, i.e., higher the intensity, lesser the cure.

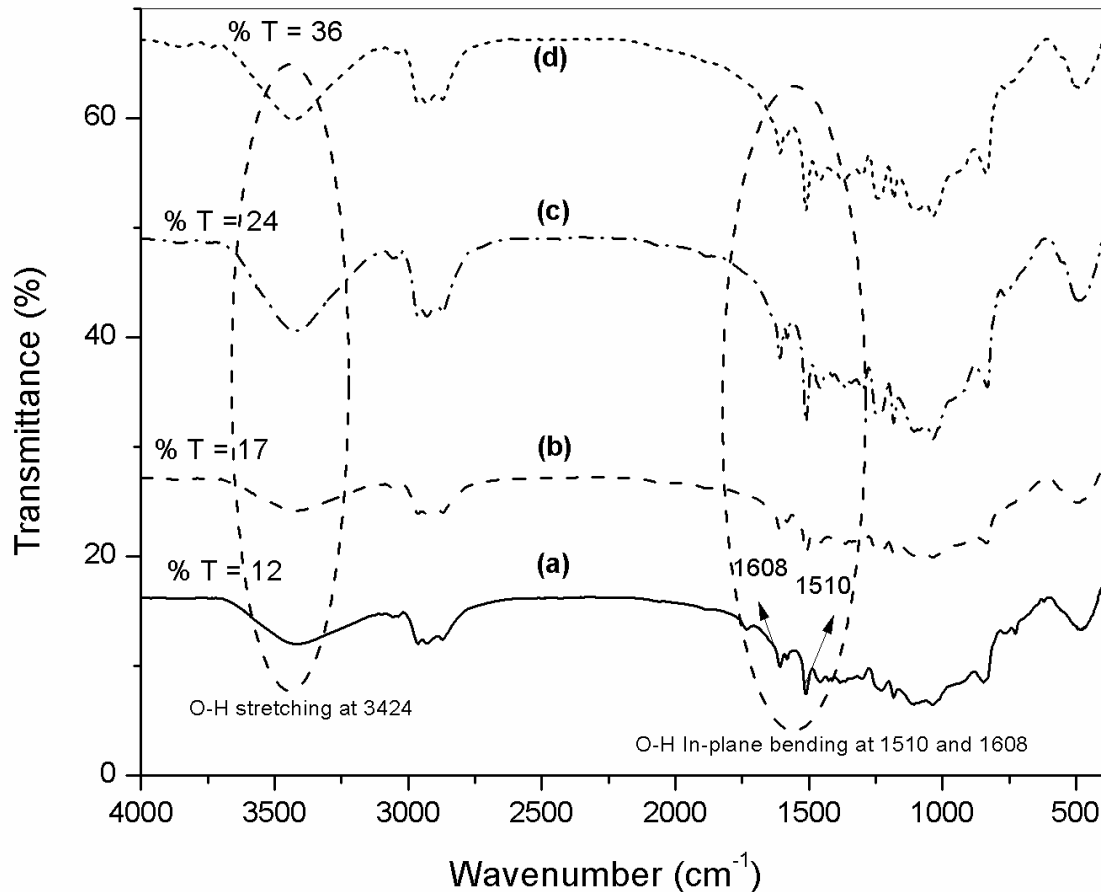


Figure 5.8: Changes in the FTIR spectra of EP GFRP composites during SW aging for (a) 0 days; (b) 15 days; (c) 30 days and (d) 90 days

Interestingly, the SW-conditioned and unaged specimens do not show much difference in the wavelength of peaks identified; however, there is a significant difference in the intensity of peaks recorded. In Figure 5.8, it can be seen that as more water is absorbed, it tends to occupy the free spaces in a material, thus undergoing chemical interaction with an epoxy matrix which, is verified by the increased intensity of the peak. Thus, it can be stated that as immersion time

increases, the intensity and shape of the O-H stretching band (at 3424 cm^{-1}) also increase. Further, the wide range of vibrational bands in the range of $3900 - 2800\text{ cm}^{-1}$ (as shown in Figure 5.8) is due to different water absorption mechanisms by the epoxy resin. Therefore, FTIR analysis shows good correlation between the percent weight gain and the chemical interaction of water with an epoxy-amine network.

Therefore, FTIR analysis has been successful in developing a good relationship between the percent weight gain, swelling of the epoxy matrix and the chemical interaction of water with an epoxy-amine network especially for EP GFRP composites.

5.4.2.2 CNT modified GFRP composites

After analyzing the mechanical behavior of EP GFRP composites in water, it was essential to explore the similar effect for CNT GFRP composites under the same conditions. Figure 5.9 illustrates the flexural modulus, strength, ILSS and elongation (at break) properties for conditioned and un-conditioned ACNT GFRP specimens.

At a glance from Figure 5.9, it can be seen that the material lost its stiffness, from 9.9 to 4.3 GPa, within the first 15 days of aging in SW environment. But, stiffness recovered by more than 79% (i.e. from 4.3 GPa to 7.7 GPa) within 30 days, followed by a consistent 6.5 GPa modulus value as shown in Figure 5.9. A similar trend was also seen in the strength where, the maximum (205 MPa) was recorded after the mid-time aging. These results are in accordance with those given by [Prolongo *et al.*, 2012] thus suggesting that, although CNT reinforced composites absorbed less water as compared to EP GFRP composites they will tend to have a larger plasticization effect. The absorption of seawater into the matrix resulted in seawater molecules entering the interface, confirmed by traces of salt particles seen in Figure 5.10a. Also, the effect of Type (I) water as observed in EP GFRP composites seems to be similar for CNT GFRP composites. All these reasons support the drop in stiffness and strength during the initial stages of water absorption of ACNT GFRP samples [Apicella and Nicolais 1985, Nogueira *et al.*, 2001].

On the contrary, hygrothermal aging of the samples in DW initially revealed less severity, i.e., there was 16% more retention in stiffness and strength values as compared to that observed for SW. Further on prolonged aging, the modulus remained almost same, whereas the

strength showed an improvement of 8% as compared to the control sample (refer to Figure 5.9). This phenomenon was also observed by Zhou and Lucas from Dynamic Mechanical Thermal Analysis (DMTA) analysis after immersing samples for a long time [Zhou and Lucas 1999]. Such varying behavior is ascribed to a change in the mechanism of water absorption [Carter and Kibler 1978, Popineau *et al.*, 2005, Prolongo *et al.*, 2012]. During the initial stages, the diffused water induces plasticization of the resin, thus lowering the glass transition temperature, strength, and stiffness of the composite. But, as the aging time increases, water uptake also increases and tends to reach a saturation level, approximately around 1500h (as shown in Figures 5.2 and 5.3). These water molecules tend to build secondary hydrogen bonding with unreacted epoxide and amines present in the matrix (from amino-CNTs) and thus enhance the interfacial adhesion and result in the recovery of the mechanical strength.

Figure 5.9 also depicts higher ILSS and strain at break values for aged samples as compared to the unaged sample for all durations. A significant increase of 52% in ILSS and 38% in elongation at break was recorded after 15 days of conditioning and reported further increase by mid-time for SW environment. A similar behavior was also seen in samples conditioned in DW environment. There are a few possible reasons that support this behavior. Firstly, the deposition of sea water moiety onto the glass fibre surface prevented the fibre delamination during the application of an external load. Also, the matrix crack propagation followed a tortuous path, likely due to the presence of CNTs in the matrix as shown in Figure 5.10b. The deviation of the crack from its original path shows the stiffness of nanoparticles strongly adhered to the epoxy matrix that justifies the experimentally obtained higher mechanical properties of the composites even after exposure to water for 720 h (30 days) [Ayatollahi *et al.*, 2011, Prolongo *et al.*, 2012]. Also, it might be due to the formation of covalent bonds between the glass fibre surface, amino-CNTs dispersed in resin and seawater molecules (as it contains primarily Na^+ and Cl^- ions) lying in the composite interface [Chakraverty *et al.*, 2013, Mourad *et al.*, 2010].

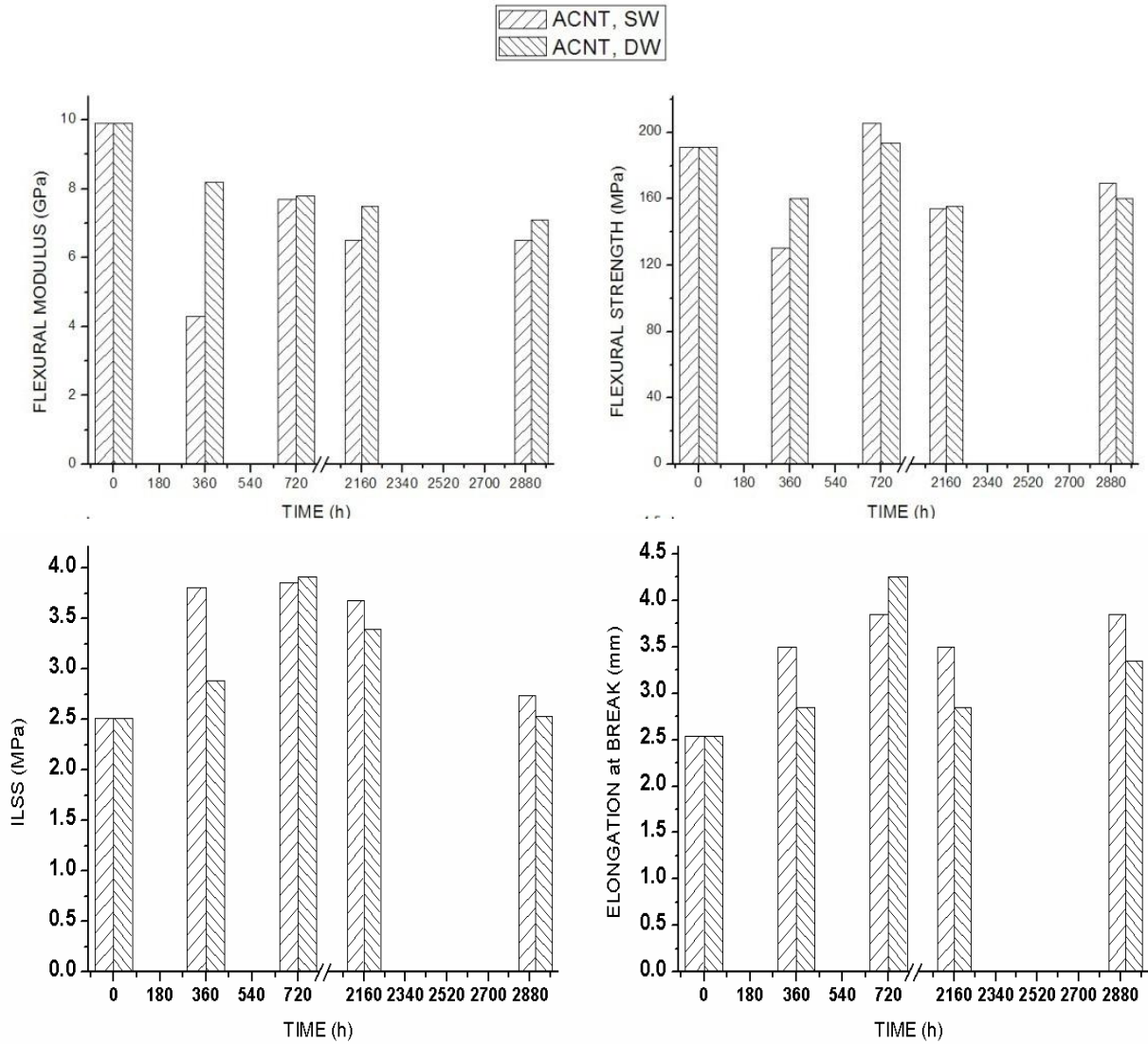
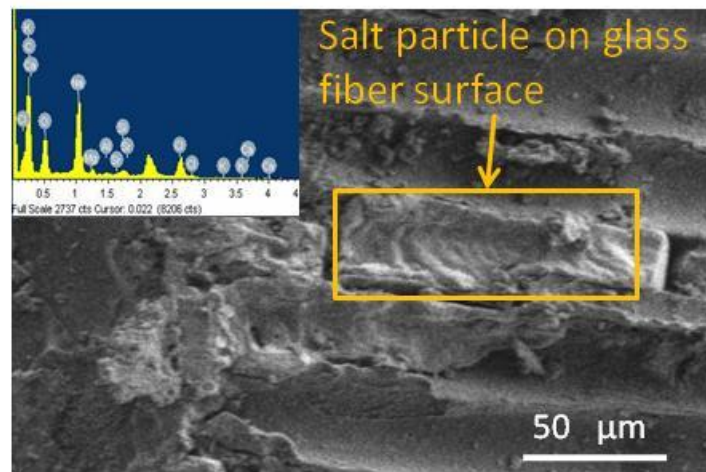


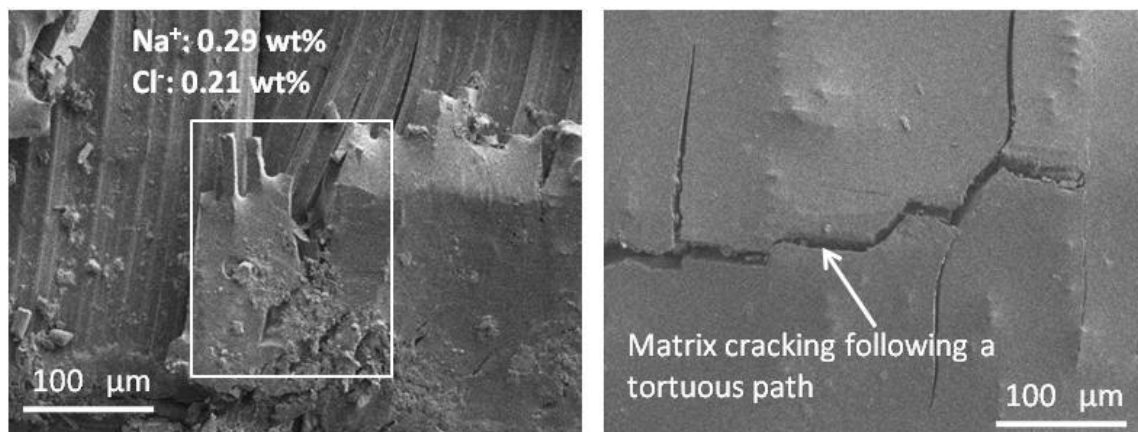
Figure 5.9: Effect on flexural properties of ACNT GFRP specimens after immersion in SW and DW for increasing aging time

On the contrary, further immersion in seawater up to 2160h(60 days) deteriorates the fibre-matrix interface as evident by fibre debonding of individual fibre plies and matrix cracking at various sites (refer to Figure 5.10c) as compared to the unaged specimen, which confirms the plasticization effect of resin. Plasticization caused swelling of the matrix and hydrolysis which further deteriorated the fibre-matrix interface, thus lowering the strength, stiffness, and ductility of the composite. Interestingly, the ILSS and elongation at break properties deteriorated maximum by 9% for SW but, it was significantly more in DW environment.

(a) 360h/ 15 days



(b) 720h/ 30 days



(c) 2160h/ 90 days

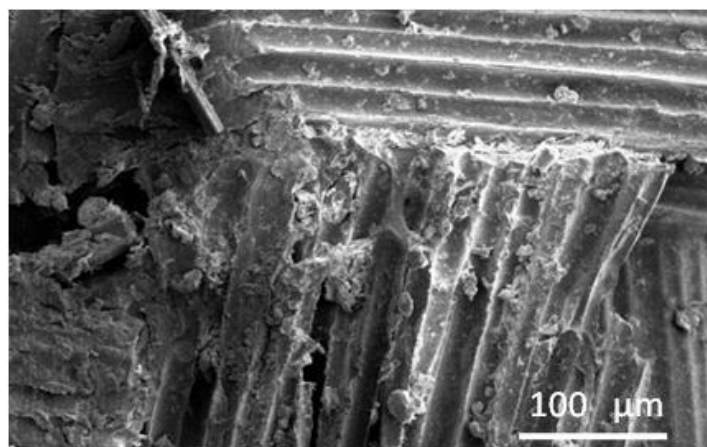
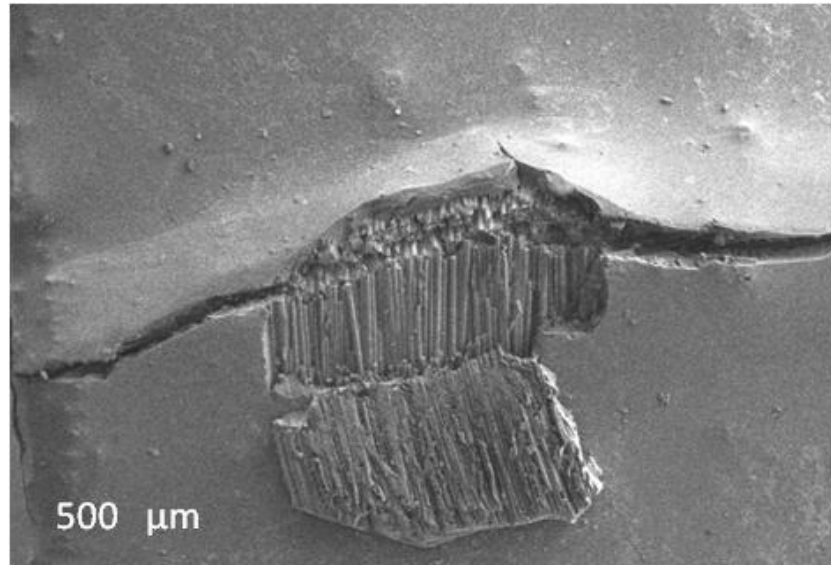


Figure 5.10: SEM image illustrating the morphology of ACNT GFRP specimens after aging in SW for 15, 30 and 90 days

Aging of ACNT GFRP samples in distilled water proved to be more harmful because of the extra water absorbed into the interface. As the flow of water increased, it attempted to wash away the obstructions (such as glass fibre surface) in its path as shown in Figure 5.11a.

(a) 720h/ 30 days



(b) 2160h/ 90 days

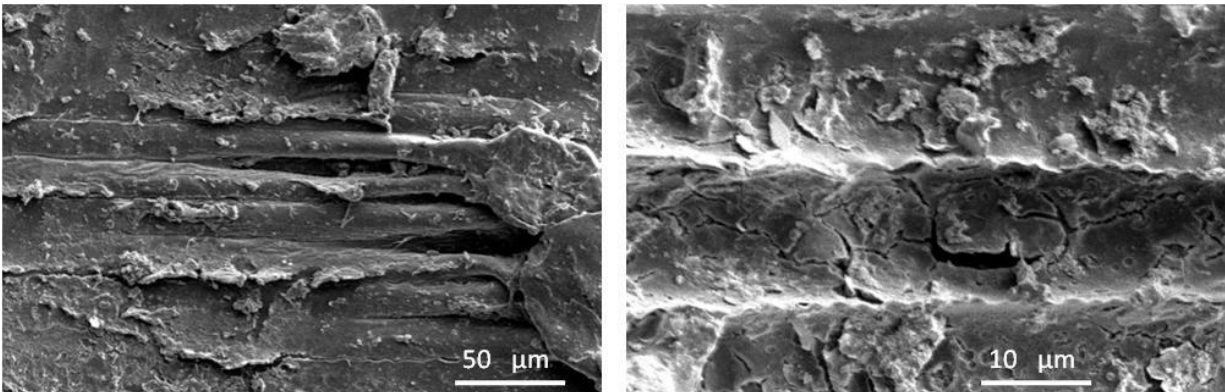


Figure 5.11: SEM image illustrating the morphology of ACNT GFRP specimens after aging in DW for (a) 30, (b) 90 days

Also, after immersion for 90 days, it can be seen that the fibres reveal a coarse surface depicting high deposition of particles and cracks in the fibres at various instances (as shown in

Figure 5.11b), which is possibly due to poor interfacial bonding between the fibres and the matrix. As a result of these factors, the flexural strength, strain, and interlaminar shear strength of the composite plunged. Further conditioning of these samples in SW and DW, i.e., up to 2904h (121 days) revealed a recovery in strength and strain at break, while the ILSS properties continued to deteriorate.

Therefore, from the above findings, it can be stated that the presence of amino group (which is amino-CNT here) in the epoxy matrix showed higher affinity of water absorption as compared to EP GFRP specimens that are fully cured and hence lacking extra amino groups. The amino groups reacted with hydroxyls of water, which reduced the stiffness and strength initially, but after reaching a saturation level, there was transformation from Type I (water) to Type II (water) [Prolongo *et al.*, 2012]. It means that water molecules change from being bonded by one hydrogen bond (Type I) to form multiple chemical connections (Type II). As a result, Type II water no longer acts as a plasticizer; instead, it promotes the secondary crosslinking with hydroxyl groups of epoxy resin such as hydroxyls and amines. This mechanism, possibly explains the recovery of mechanical properties after conditioning for longer time in water and/or moist environment. In conclusion, it can be stated that the degradation in mechanical properties in the post saturation period is considerably lesser as compared to that observed during pre-saturation period [Muthirakkal *et al.*, 2010].

5.4.2.2.1 PCNT GFRP composites

Previously in Chapter 3, the addition of pristine nanotubes (PCNT) in epoxy resin had shown better mechanical properties for the dry specimens as compared to the ACNT GFRP [Garg *et al.*, 2015]. However, studies reporting their performance after hygrothermal aging are scarce. For this purpose, it has been considered to study the aging effect of these samples when immersed in SW and DW. These samples were weighed after every 2 days for determining the absorption behavior, but, were tested finally, after 121 days under 3-point bending mode. The average of four samples tested has been listed in Table 5.5.

From Figures 5.2 and 5.3 it could be observed that the water absorption mechanism for PCNT samples was quite different than that of ACNT. Firstly, in SW environment, the maximum water content of 2.6% was attained after 55 days immersion time for PCNT as

compared to 18 days observed for ACNT samples. Secondly, after a few days only the PCNT samples approached the equilibrium level of approximately 2%. A similar trend was also observed for PCNT samples aged in DW, but the maximum water content attained after 55 days was significantly lower (2.15%). Further, the mechanical test results for these samples after conditioning for 2904h (121 days) in SW and DW have been listed in Table 5.5.

Table 5.5: Summary of change in mechanical properties of PCNT GFRP composites after 2904h (121 days) of aging in SW and DW

S. No.	Type of Water	Flexural Modulus (MPa)	Flexural Strength (MPa)	Elongation at break (mm)	ILSS (MPa)
1.	Reference (unaged)	10900	229.33	7.83	3.01
2.	SW	5482.5	121.5	2.9	3.272
3.	DW	3907.5	109.25	3.45	3.332

In general, the flexural properties deteriorated except interlaminar shear strength that showed an increase. Samples exposed to SW environment revealed approximately 50% drop in stiffness and strength, while the strain was reduced by 63%. This suggests the continuous deterioration of the bonding between the fibres and the matrix as more water ingressed into the composite. On the contrary, although the amount of distilled water absorbed into the interface was lower but, it caused higher plasticization effect. As a result, a drop of 64% and 52% was calculated for stiffness and strength, respectively. A higher drop in modulus for DW samples, due to plasticization of the matrix, is supported by a better strain at break value as mentioned in Table 5.5. On the other hand, ILSS properties enhanced possibly due to the mechanical interlocking at the fibre-matrix interface and relaxation of residual stresses within the composite interface.

However, an overall analysis reveals a significant effect on all the mechanical properties studied as compared to the reference (unaged) sample thus, suggesting that the diffusion of water inside a non-functionalized nanotube glass fibre composite is more devastating, possibly due to

the absence of strong covalent bonding between the nanotubes and epoxy resin. Although the water uptake content was significantly lower than other EP GFRP composites studied, their effect was more profound specifically for the damages introduced to the fibre/matrix interface.

Lastly, a comparison of the flexural properties has been carried out between ACNT and PCNT samples conditioned in the same SW environment studied over different time intervals of 15,30, 90 and 121 days (as shown in Figure 5.12).

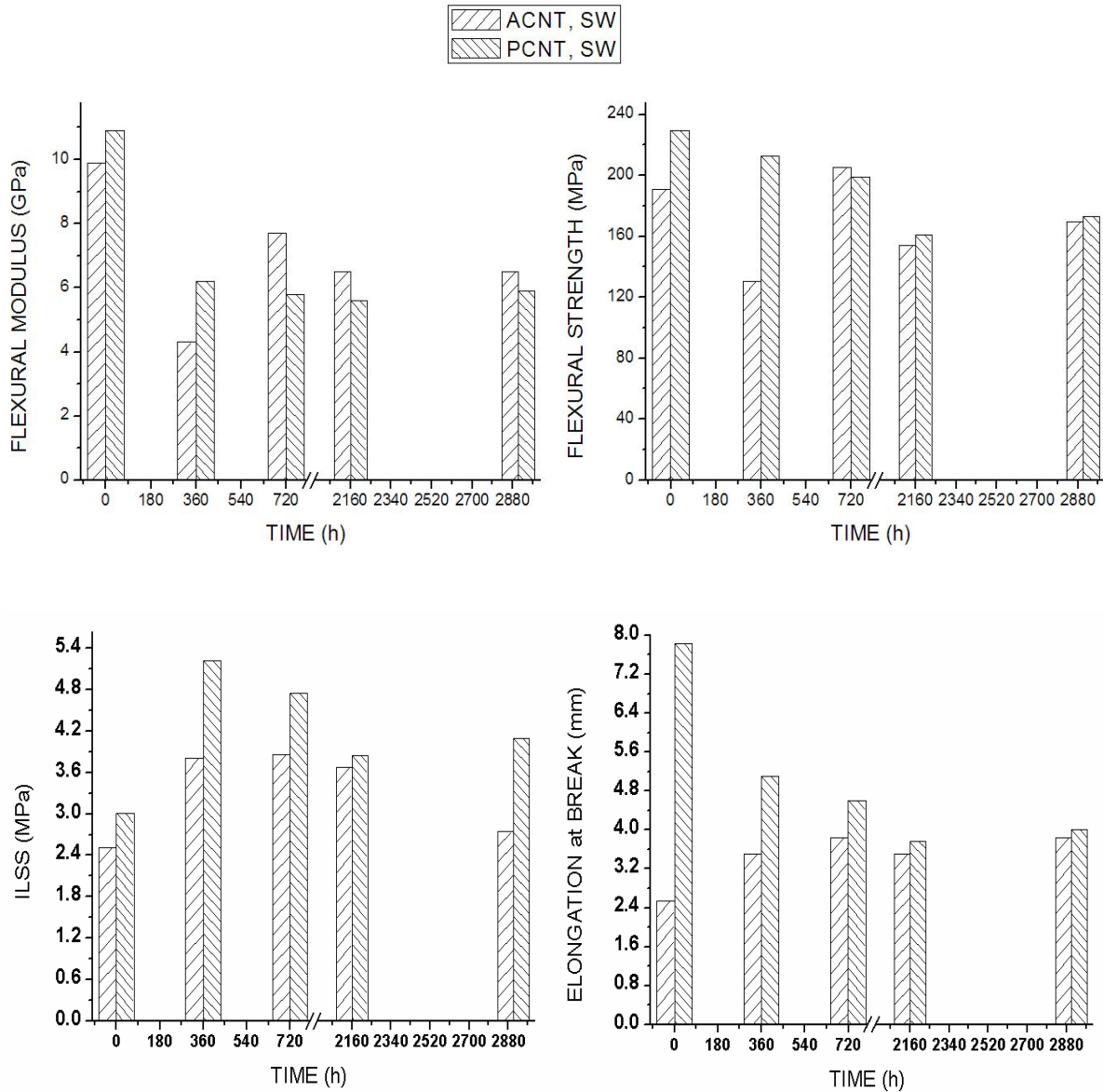


Figure 5.12: Comparison between flexural properties of ACNT and PCNT GFRP samples after aging in SW for different immersion times

In general, PCNT samples have demonstrated a continuous retarding effect on the stiffness, strength and strain at break properties up to 2160h (90 days) aging duration. The significant reduction in modulus is because of losing bonding strength between the fibres and the epoxy matrix. Whereas, the drop in flexural strength is likely due to the absorbed water content that damaged the fibre layers. Also, the pristine nanotubes did not have any functional groups attached on to its end-walls, which suggest that as water ingresses it attacks the matrix followed by the fibres. Whereas, the drop in strain highlights the brittle failure of the material since the fibres were unable to sustain external stress for longer durations. On the contrary, ACNT samples demonstrated a recovery in properties after 720h of exposure as discussed previously. After conditioning for another 60 days (i.e. up to 90 days) both PCNT and ACNT samples show a slight drop which suggests the development of cracks and fibre debonding. Also, the presence of NaCl and other sea water particle clusters in the interface and on the fibre surface aided in minimizing the effect of external stress applied.

Lastly, the Interlaminar shear strength of ACNT and PCNT samples is observed and it is found that during the first 15 days, there was an increase by 52% and 73% for ACNT and PCNT samples, respectively. However, after 30 days conditioning, ACNT samples showed a further increase, whereas, a drop was seen in PCNT samples. Following this, both the samples continued to show a decreasing trend for the next 60 days. But at the end of 121 days aging, the value of ILSS was 36% more for PCNT and 9% in the case of ACNT as compared to their respective unaged samples. This behavior can be explained by observing the morphology of the PCNT sample as shown in Figure 5.13.

From Figure 5.13 large deposition and huge clusters of simulated seawater particles such as Mg^{2+} , Zn^{2+} , Sr^{2+} , Na^+ , Cl^- (confirmed by EDS spectra) scattered throughout the interface was seen. In addition to this pieces of fibre-matrix interface were also observed under SEM. As a result, there was transformation of covalent chemical bonds into physical interactions via the formation of hydrogen bonds between glass fibres, water molecules, and scattered pristine nanotubes.

In summary, PCNT samples exhibit similar values as ACNT for stiffness, strength, and strain at break after 121 days aging duration in SW. But, considering the percent change in all flexural properties, the recovery mechanism, and morphology observed for ACNT samples, it

can be concluded that ACNT GFRP samples perform better under hygrothermal conditions. In addition to this, the incorporation of CNT in GFRP samples quantitatively lowered the water content and reduced the diffusivity coefficient due to its high barrier properties and strong bonding with the epoxy matrix.

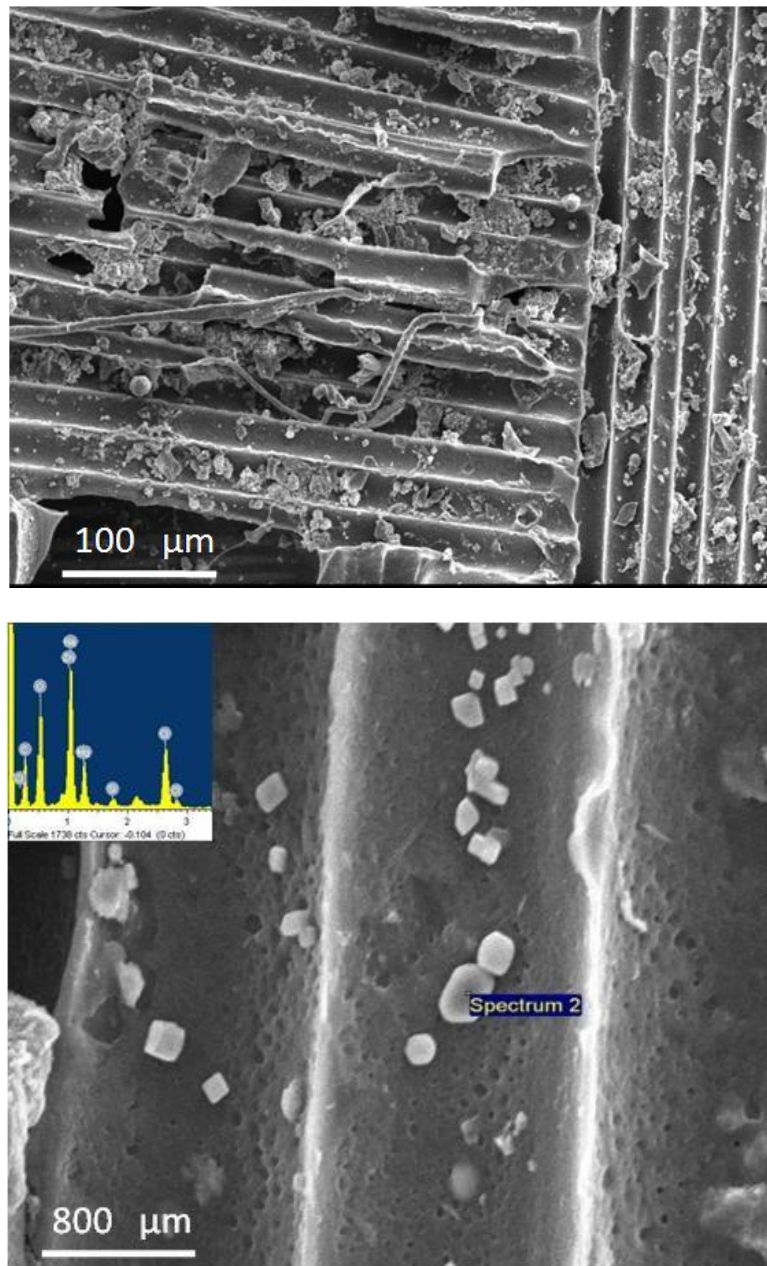


Figure 5.13: Morphology of hygrothermal aged specimens after 2904h (121 days) for PCNT GFRP samples

An extension of the above hygrothermal study involved a further reduction in the amount of water uptake in GFRP composites by introducing another coating on the edges of the sample instead of the addition of high nanofiller content.

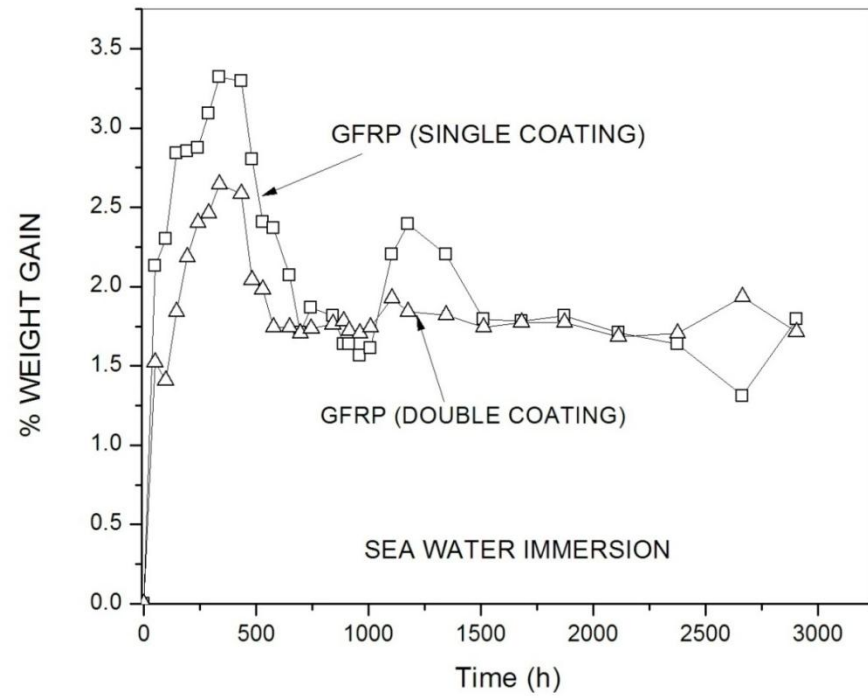
5.4.3 Effect of edge coating on water infusion behavior for GFRP samples

All the samples subjected to hygrothermal conditioning prior to this study were coated with a single thin layer of epoxy on the edges to allow the water absorption through the surface only. The experimental results revealed significant water uptake content for EP GFRP composites in a short interval of time. In order to study this water absorption mechanism in depth and to alleviate excess water sorption another set of samples were prepared that incorporated double coating (DC) of samples. Subsequently, a comparison was made by analyzing their diffusion and mechanical behavior with single coated (SC) specimens after exposure in SW and DW at 25°C.

For the first time, EP GFRP samples with double edge coating were subjected to hygrothermal conditions and these are referred to as model composites in the discussion ahead. It is hypothesized that these specimens would show even further lower water sorption under both SW and DW environments and make the composite material more durable, while retaining their properties during their in-service conditions. Figure 5.14 (a and b) compares the diffusion curves between single and double coated EP GFRP samples when immersed in SW and DW, respectively.

For the model composite, the water absorption mechanism is similar to that observed previously for EP GFRP samples with single edge coating. The maximum weight gained (M_{∞}) by the model composite specimens was 2.64% and 3.93% after 14 days of immersion in SW and DW, respectively. The diffusivity rate of model composites in SW and DW were calculated to be $2.286 \times 10^{-7} \text{ mm}^2/\text{s}$ and $3.539 \times 10^{-7} \text{ mm}^2/\text{s}$, respectively. Hence, on comparing these values with earlier results, there is 20% less water content and the seawater diffused at 46% lower rate into the composite. This indicated that the absorption of water is further restricted and it also reduces the possibility of water seepage through the exposed edges. As a result of lower water content, it would cause less plasticization of the matrix and consequently more retention of the stiffness and strength properties.

(a)



(b)

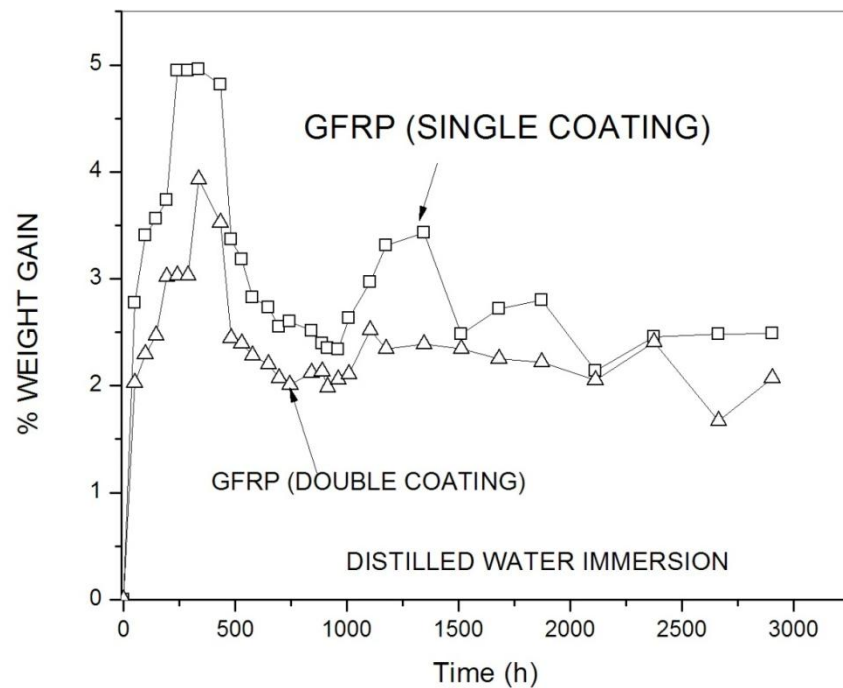


Figure 5.14: Diffusion curves of EP GFRP composite (single and double epoxy coated) specimens immersed in: (a) SW, (b) DW

Figure 5.15 shows the mechanical performance of EP GFRP samples with SC and DC as compared to unconditioned EP GFRP sample after conditioning for 2904h (121 days) in SW. Following observations were drawn after analyzing the trend in Figure 5.15: (i) the modulus and flexural strength of the DC samples dropped by 43% and 29%, respectively and (ii) the elasticity and ILSS properties showed a minimal descend by 5% and 2% respectively, as compared to SC sample.

On the other hand, DC specimens in DW illustrated a noteworthy decrease for all the properties studied vis-à-vis SC specimens. Table 5.6 summarizes the mechanical properties for unconditioned and conditioned EP GFRP specimens in DW at the end of 121 days. It can be seen that the flexural modulus, strength, ILSS and strain values plunged by 55%, 43%, 22% and 15%, respectively vis-à-vis SC specimens.

Table 5.6: Summary of the mechanical properties of EP GFRP samples after hygrothermal conditioning in DW for 121 days

Type of sample	Flexural Modulus (GPa)	Flexural Strength (MPa)	ILSS (MPa)	Strain at break (mm)
EP GFRP – unconditioned	7.3	131.33	1.81	2.9
EP GFRP, SC	7.4	165.67	2.61	3.8
EP GFRP, DC	3.3	94.7	2.04	3.23

The mechanical behavior of DC specimens is contrary to the expected results as it showed further deterioration of properties on comparing with single coated EP GFRP specimens. To carry this analysis further an explicit study of SC and DC of specimens is examined for the SW immersion of ACNT GFRP specimens.

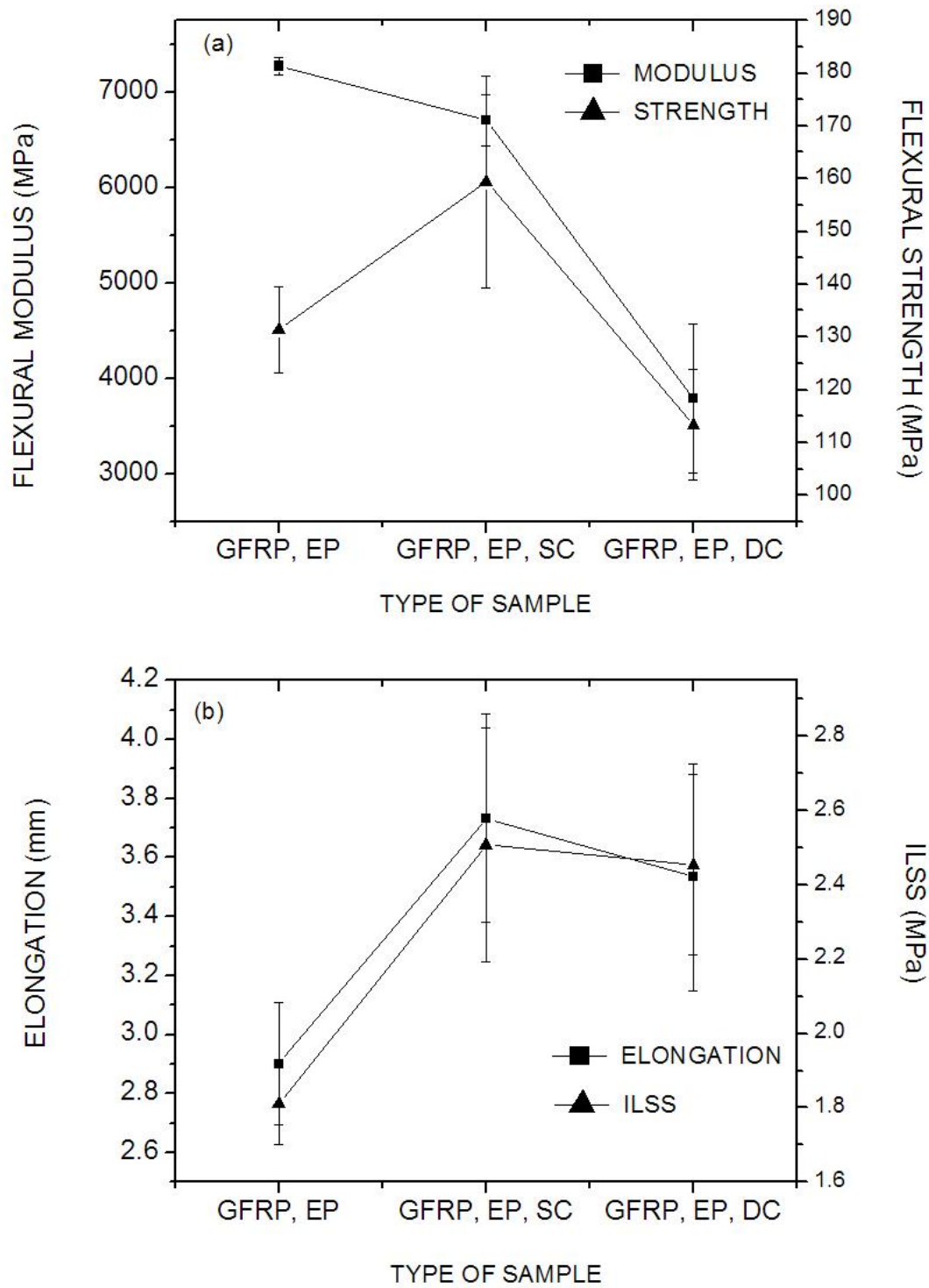


Figure 5.15: Comparison of mechanical properties for EP GFRP composites (SW) – single versus double edge coating

5.4.3.1 Effect of edge coating on ACNT GFRP composites

For this rationale, a comparative analysis has been carried out for ACNT GFRP composites with single and double coated samples when exposed to SW at 25°C. The experimental results obtained from the water infusion behavior are depicted in Figure 5.16.

Figure 5.16 represents the weight gained by both single and double edge-coated ACNT GFRP specimens versus the immersion time.

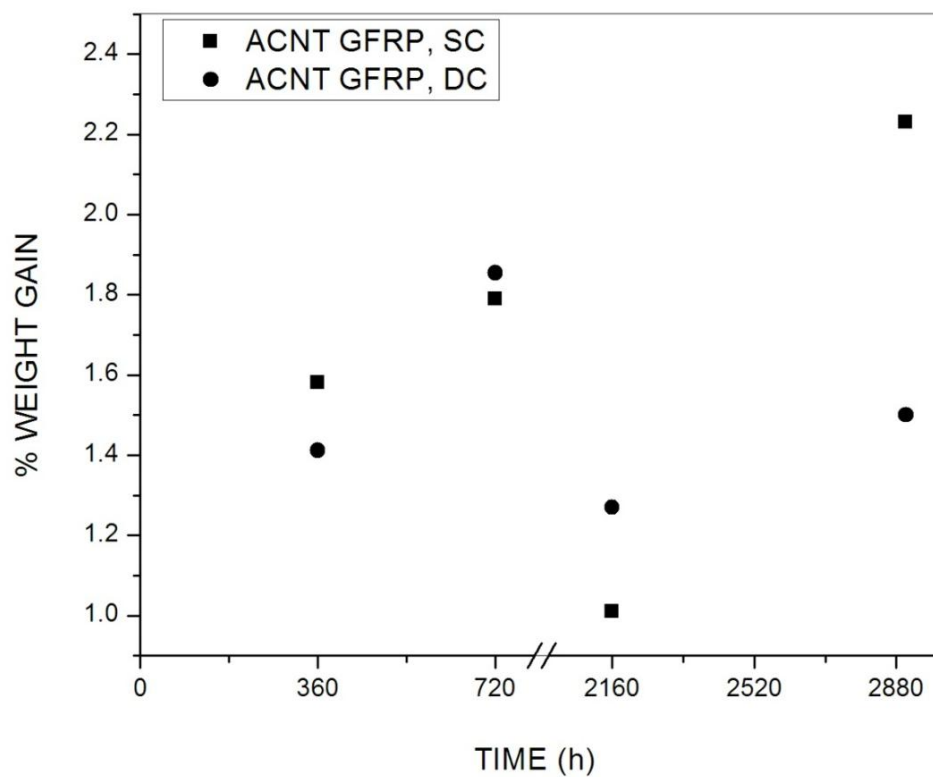


Figure 5.16: Diffusion behavior of ACNT GFRP samples (SW) with single and double edge coating

It can be clearly seen that both the samples follow the similar trend (as reported in section 5.4.1.1) i.e. maximum diffusion of water into the composites occurs within first 30 days of immersion, followed by a drop during the next 60 days and then again a sharp increase after 30 days of conditioning. Once again, double edge coated ACNT GFRP samples have illustrated lower water intake as compared to single coated specimens while maintaining same

environmental conditions. From the figure it can be analyzed that an extra coating on the edges does affect the water content but, still shows a varying trend. Clearly, the % weight gain for DC ACNT GFRP samples was higher than SC ones at 30 and 90 days interval. Figures 5.17 and 5.18 illustrate the mechanical behavior of hygrothermally aged ACNT GFRP samples having single and double coating, respectively. Figure 5.17 presents the mechanical behavior of single coated ACNT GFRP specimens with their detailed explanation stated earlier in Section 5.4.2.2. Thus, the behavior of DC samples as presented in Figure 5.18 with increasing immersion time has been discussed ahead.

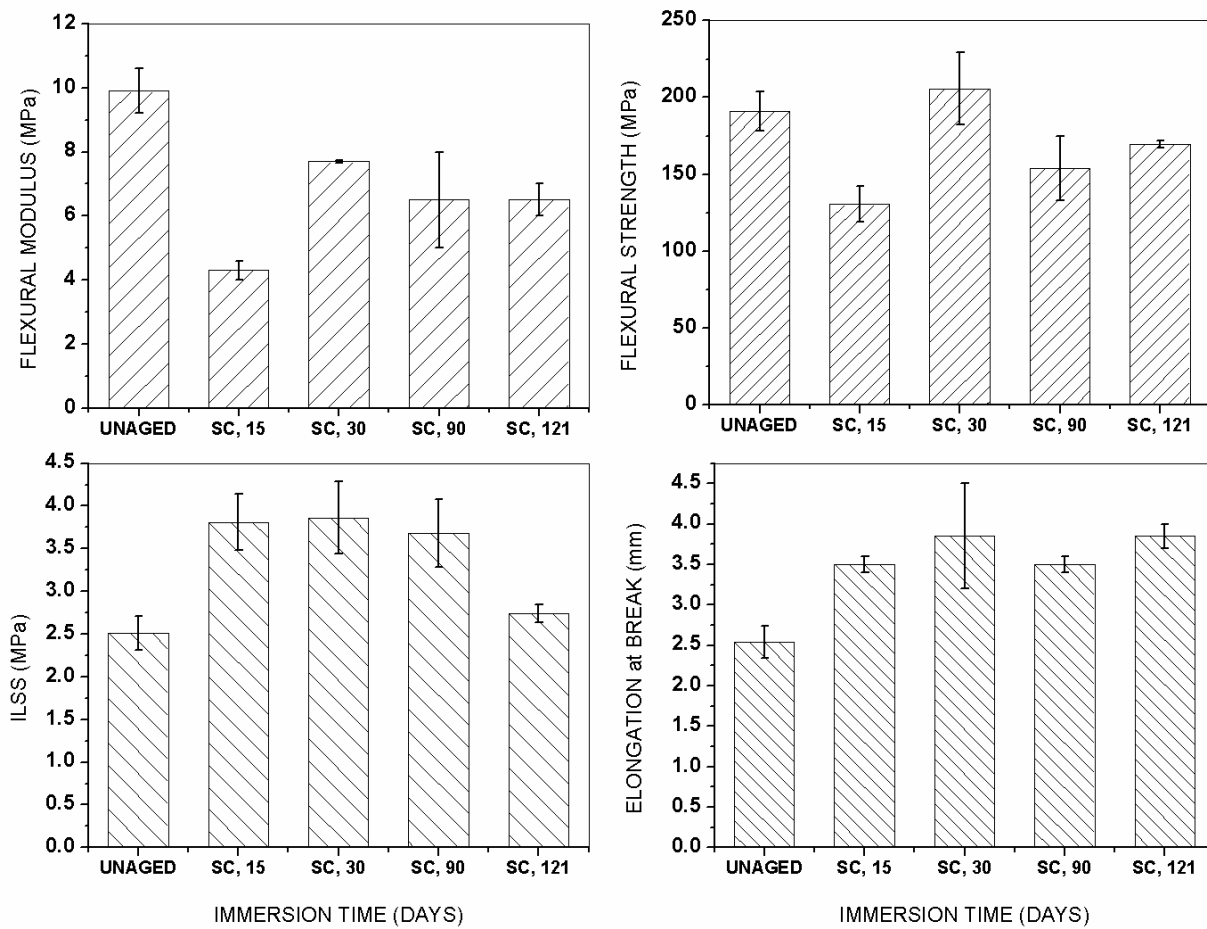


Figure 5.17: Mechanical behavior of ACNT GFRP, SC samples (SW) with immersion time up to 121 days

Interestingly, for the DC samples, the initial increase in weight gain was due to concentration driven absorption mechanism that resulted in non-homogeneous flow of water

throughout the matrix. As a consequence, it created localized defects which act as region of defects and thus lowered the strength by 33% within 15 days of immersion. Subsequently, for the same time period water uptake caused plasticization of the epoxy matrix that resulted in lower modulus and higher strain values as seen in Figure 5.18.

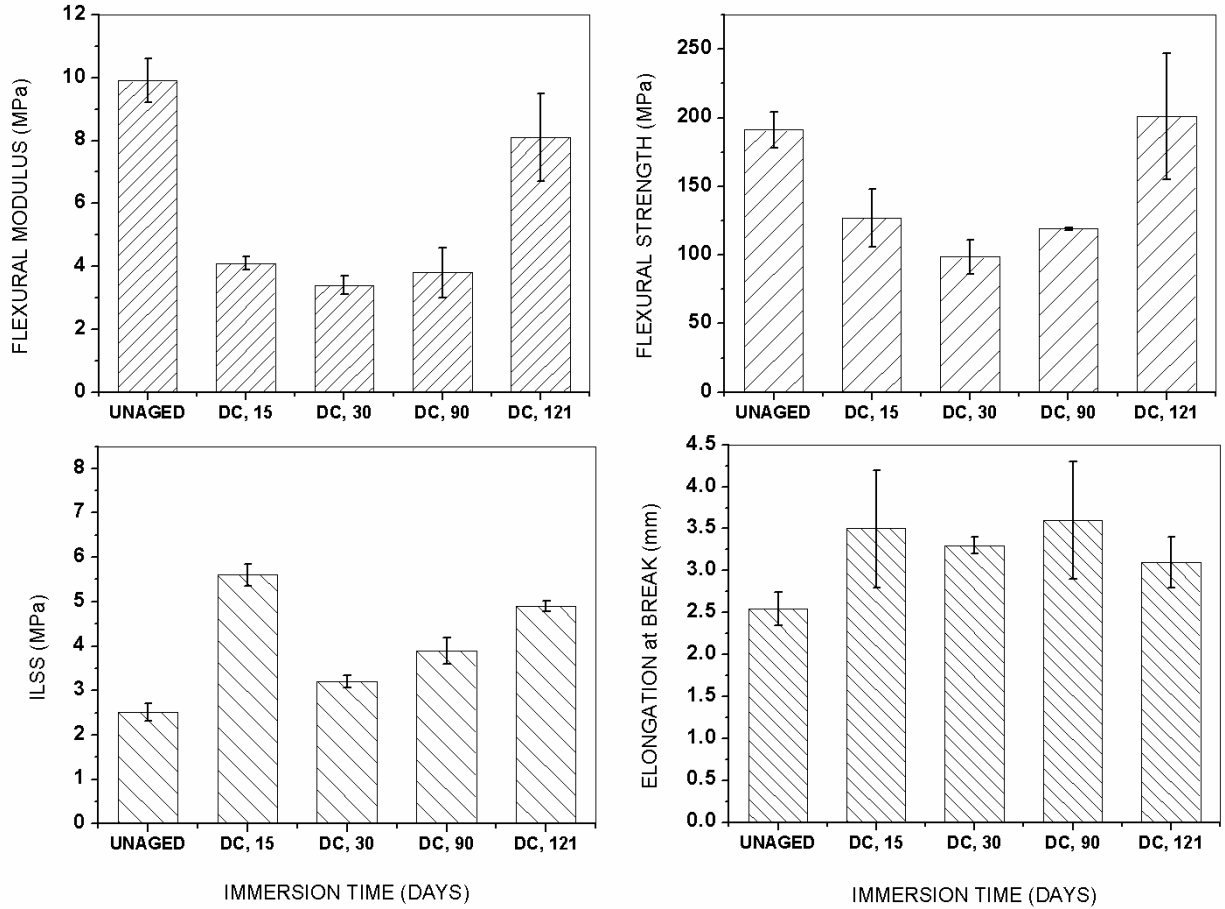


Figure 5.18: Mechanical behavior of ACNT GFRP, DC samples (SW) with immersion time up to 121 days

However, on prolonged SW immersion it is likely to cause mechanical property deterioration concomitant to plasticization and swelling, leading to interfacial debonding and assisting in further moisture uptake. The same phenomenon has been witnessed for 30 days conditioned samples. Since, the water content inside the interface was increased it resulted in the swelling of the matrix and a subsequent increase in modulus and decrease in strain values occurred. Also, the strength of the material recovered probably due to the relaxation of residual stresses. The recovery of mechanical properties seen at long aging times is probably due to Type

I and Type II water, which has been discussed earlier in this chapter for single coated ACNT GFRP samples.

Furthermore, as observed for strain at break, the interaction of seawater molecules assists in improving the ILSS properties of the samples. The improvement is probably due to the SW molecules inhibiting the delamination crack growth progress as was seen previously in SC ACNT GFRP samples. Also, the strong bonds between amino-CNTs dispersed in resin with glass fibre acts as a bridging mechanism during the flexural loading conditions and resist the failure of the fibre-matrix interface. Lastly, an interesting observation was that after 121 days of immersion, stiffness, strength and ILSS properties have recovered for DC specimens, whereas SC samples showed a negligible change in the properties as compared to samples aged for 90 days.

Hence, as observed earlier for EP GFRP samples, the ACNT GFRP specimens with single coating have scored over double coated specimens with respect to its mechanical behavior. Whereas, considering the kinetics of water absorption behavior double coated specimens have proven to be more beneficial for hygrothermal aging in water at room temperature. The possible reasons to support these observations are yet to be examined and shall be investigated in the near future.

5.4.4 Degradation of composites at different temperatures

In the previous sections, the hygrothermal behavior was investigated for different GFRP composites on immersion in SW and DW at 25°C, since this temperature corresponded to the actual seawater temperature for most parts of the world. But, for laboratory and research purposes, exposure at elevated temperature allows to investigate the same effect, but in a shorter time span which can be used for predicting its longevity. It is known from the literature that a 10°C rise in temperature causes a doubling of diffusion rate, so exposure at 55°C would correspond to an eight times acceleration as compared to 25°C aging temperature. More detailed analysis of the same is discussed ahead.

5.4.4.1 ACNT GFRP composites at 55°C and 25°C temperatures

As mentioned above, to observe the accelerating absorption mechanism, ACNT GFRP samples (with single edge coating) were left for conditioning in the SW at 55°C for 15, 30 and 90

day period. In general, the exposure of composite materials in warm environments causes excess water intake and on prolonged aging results in material degradation to a higher extent as compared to room temperature exposure.

The recorded weight gain of the aged samples showed an increasing trend from 0.76 (after 15 days) to 1.56 (after 30 days) and 3.19% (after 90 days) after aging at an elevated temperature. This was expected because at elevated temperature water molecules have higher energy and tends to flow from higher concentration (outside the sample) towards lower concentration (inside the composite interface) and this absorption behavior shows an increasing trend versus aging time. Similar observations were made by other researchers [Mourad *et al.*, 2010, Ellyin and Rohrbacher 2000, Wood and Bradley 1997, Ray 2006, Davies and Evrard 2007, Abdel-Magid *et al.*, 2005]. The percent change in flexural properties of ACNT GFRP samples immersed for 15, 30 and 90 days at 55°C are shown in Figure 5.19. In order to calculate the percent change, the unconditioned ACNT GFRP sample was considered as a baseline data.

The flexural strength and modulus decreased by 54% and 37%, respectively at the first 15 days of conditioning whereas, the strain at failure and ILSS properties increased by 38% and 26% respectively. At 55°C, ACNT GFRP composite absorbed SW at a higher rate and this in turn led to a relaxation of residual stresses and improvement in flexural strength as seen in Figure 5.19. The modulus on the other hand, shows a maximum drop of 54% in 15 days, and then increases by 24% after 3 months of exposure to SW at 55°C. The initial reduction in modulus and increase in strain as seen in Figure 5.19 is attributed to the plasticization and ability of epoxy molecules to move freely inside the composite. Whereas, the increase in modulus over prolonged aging is likely due to swelling that improves the bonding between the fibres and the matrix. On the other hand, interlaminar shear strength (ILSS) properties were slightly affected on prolonged aging in SW at 55°C. This is likely due to the minimal effect on the strong covalent bonds between amino-functionalized nanotubes and epoxy resin as well as fibre-matrix interface that was not weakened by the warm seawater.

Thus, it can be concluded from the above discussion that the exposure of ACNT GFRP samples in a warm environment caused more than 50% loss in stiffness and strength during the first 15 days, but on prolonged aging the properties recovered. However, an overall comparative analysis clearly reveals better performance of ACNT GFRP samples at room temperature.

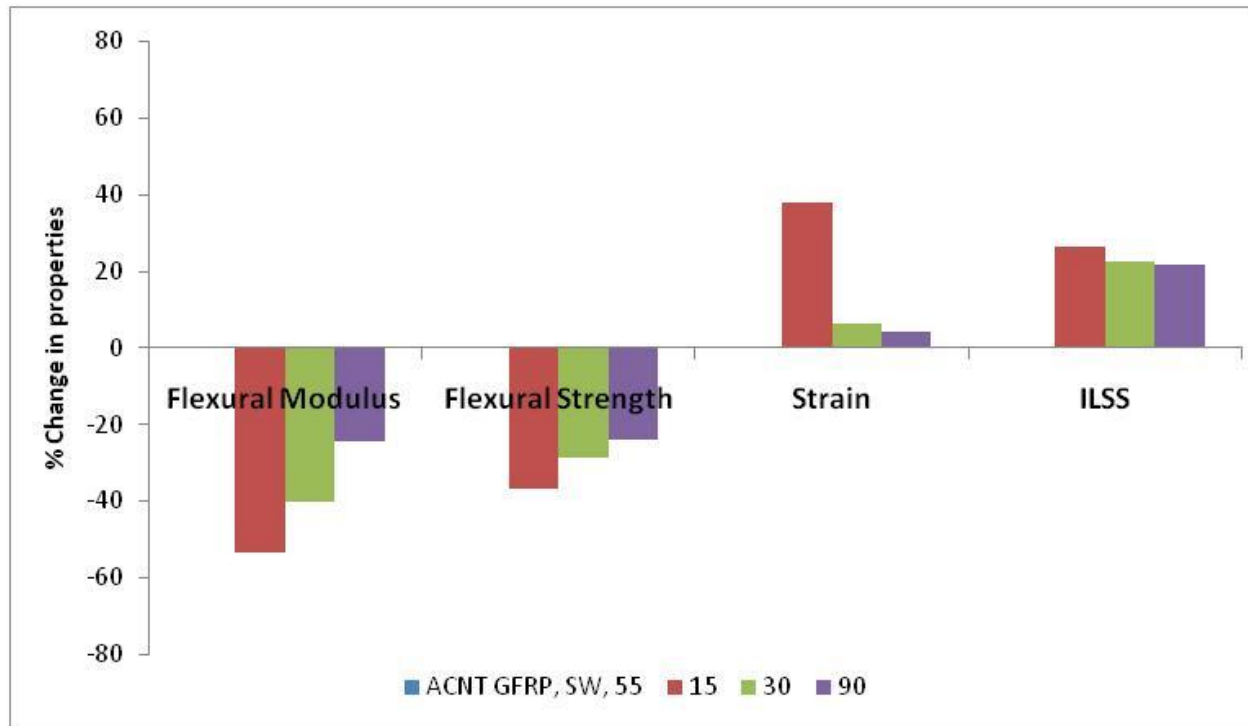


Figure 5.19: Percent change in mechanical properties of ACNT GFRP composites after 15, 30 and 90 days aging in SW at 55°C

5.4.4.2 PCNT GFRP composites at 25°C and 55°C temperatures

Considering the interesting results from the last section PCNT GFRP samples were also immersed under similar conditions as ACNT GFRP composites i.e. in SW for 15, 30 and 90 days at 55°C. The percent change in properties by aging samples at 55°C is illustrated in Figure 5.20.

The combined effect of modifying epoxy matrix with pristine nanotubes and immersion in warm environment has proven to be quite harmful in terms of material degradation. Mechanical test results illustrated that more than 50% drop in the stiffness, flexural strength, and ultimate strain of PCNT GFRP composites. The flexural modulus plunged by 62% within the first 15 days, reached 66% after 30 days, and a maximum drop of 67% at the end of 90 days aging duration. A similar increasing trend of deterioration was also visualized for flexural strength and strain at break properties.

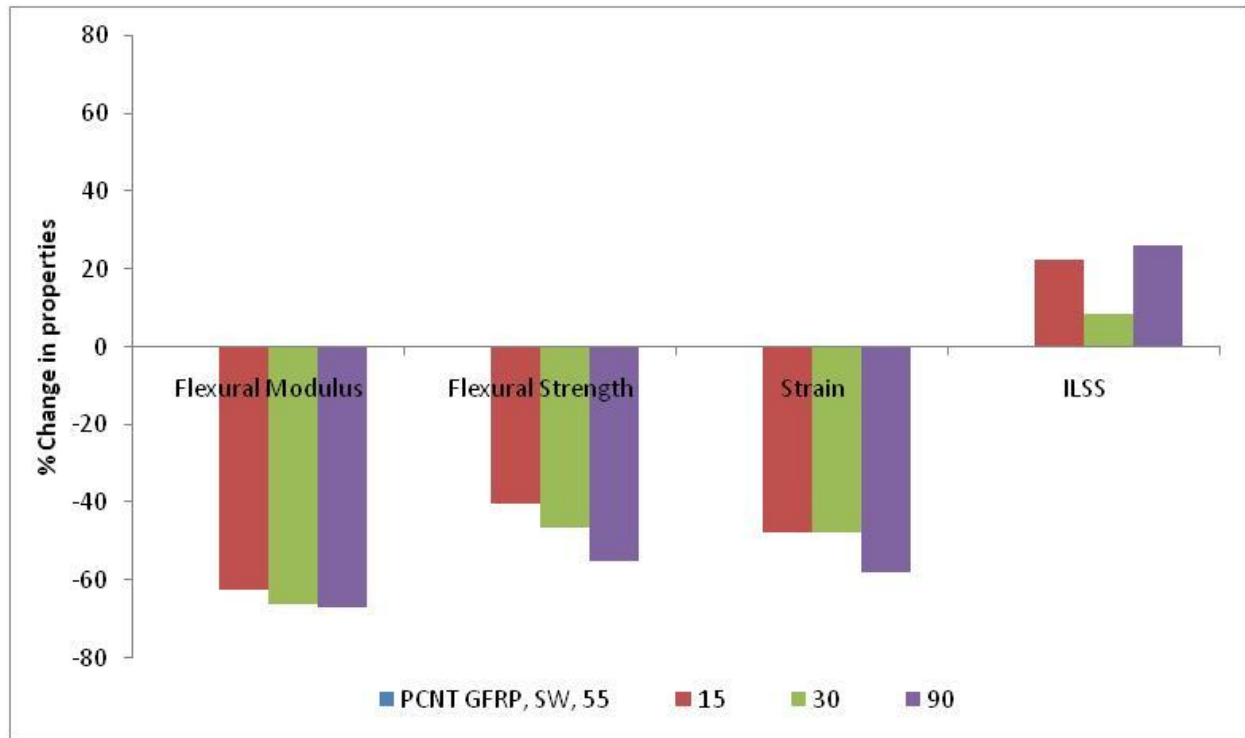


Figure 5.20: Percent change in mechanical properties of PCNT GFRP composites after 15, 30 and 90 days aging in SW at 55°C

A maximum decrease in flexural strength and strain of about 58% was observed at the end of the third month conditioning in warm seawater. Such drop usually arises due to the combined effect of plasticization and hydrolysis of the epoxy matrices as well as deterioration of the fibre - matrix interface. Similar observations and reasons have been discussed in detail for ACNT GFRP samples immersed in SW at 55°C (Section 5.4.4.1). Thus, it can be concluded that PCNT GFRP specimens have demonstrated a poor performance on exposure to SW conditions at a higher temperature, which seems to be quite catastrophic if implemented for practical purposes.

Therefore, on comparing the mechanical behavior of the ACNT and PCNT GFRP composites after exposure to same hygrothermal conditions, it can be stated that on prolonged exposure, the PCNT specimens would fail relatively quickly than ACNT GFRP samples since, the properties tend to recover in the latter case with time. Additionally, on comparing the performance of the two composites in a warm environment (i.e. Figure 5.19 and 5.20) it can be concluded that flexural modulus, strength, strain and ILSS properties are higher for ACNT than PCNT samples, when exposed to similar conditions and time period (after 90 days). A possible

reason to support the better properties of ACNT GFRP samples is due to the strong cross linked network among amino-functionalized nanotubes, epoxy resin and glass fibre mat which, is likely missing in PCNT GFRP composites.

5.4.4.3 Silane treated GFRP samples at 25°C and 55°C temperatures

Further, silane treated (ES and AS) GFRP laminates, referred to as EP ESGFRP and EP ASGFRP, were also examined for hygrothermal aging. In order to analyze the diffusion and mechanical behavior of these samples along with its durability if exposed for a longer time, the samples were immersed in the SW at 55°C for a period of 15, 30 and 90 days. A comparative analysis of %M (weight gain) among EP ESGFRP and EP ASGFRP for varying immersion time is shown in Figure 5.21. The kinetics of water absorption, indicate a pronounced effect on the quantity of absorbed water for elevated temperature as compared to that at room temperature.

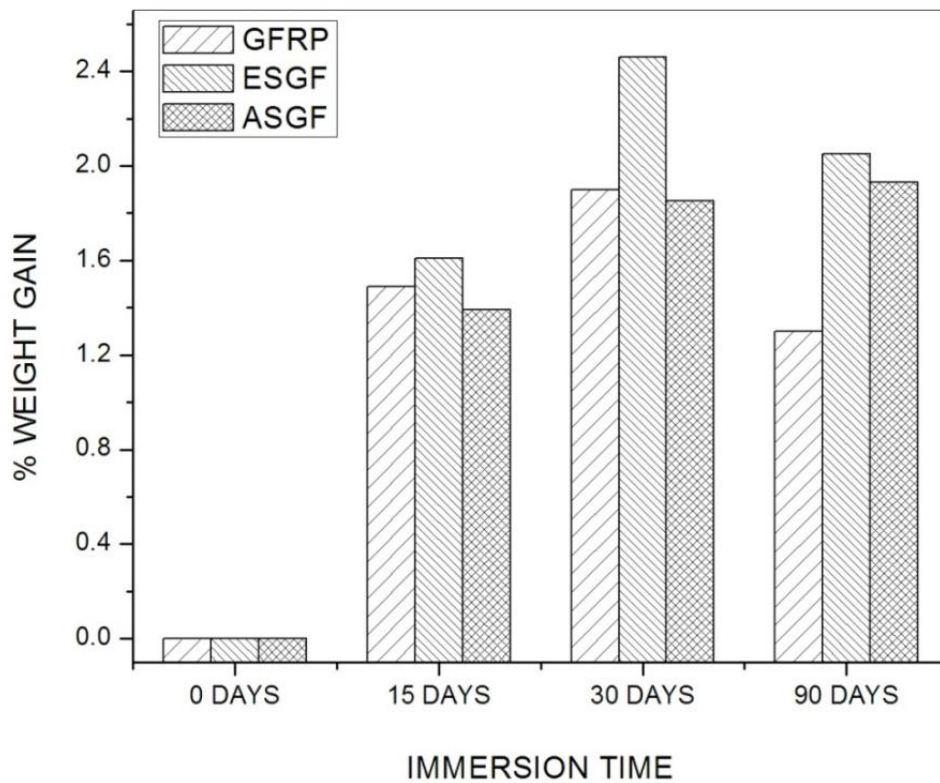


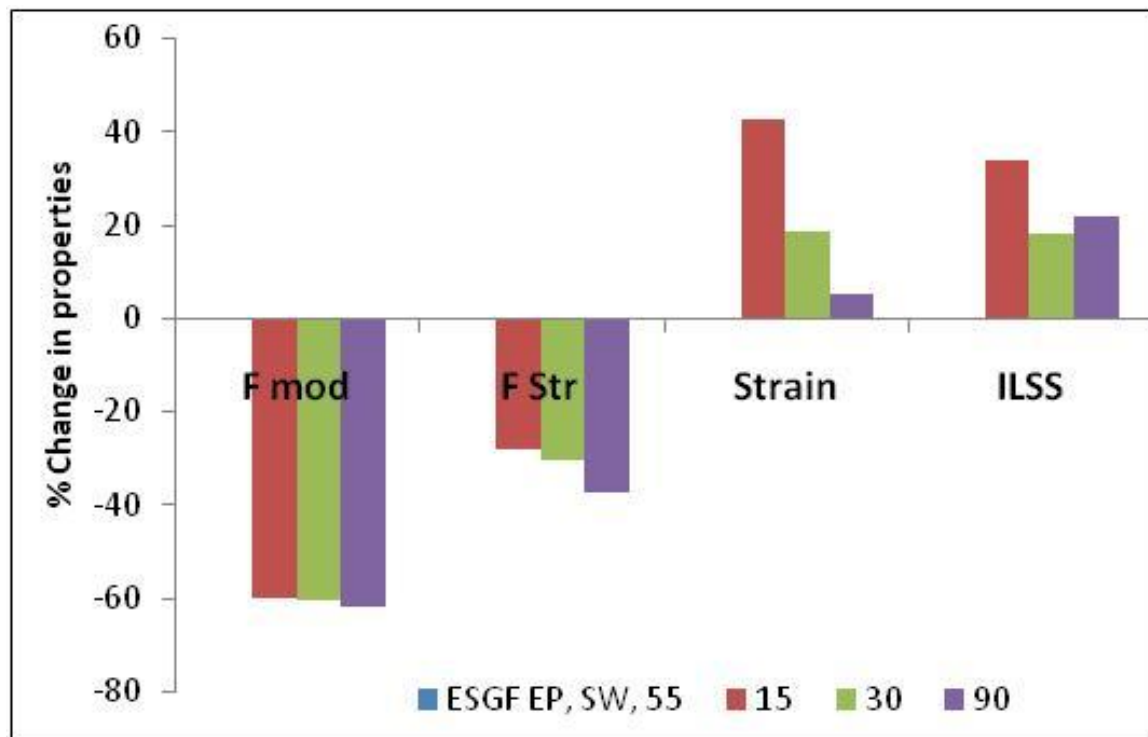
Figure 5.21: Percent weight gain by silane treated GFRP laminates for varying immersion time in SW at 55°C

From Figure 5.21 it was observed that the AR GF specimens on immersion in SW illustrate maximum water intake of 1.9% after mid-time, and then drops to about 1.3% at the end of three months. Similar behavior was seen for EP ESGFRP composites which attained a maximum water content of 2.46% after 30 days. On the other hand, EP ASGFRP composites followed an increasing trend with aging time. A maximum water content of 1.93% was achieved at the end of three months exposure to seawater at 55°C. On the whole, EP ESGFRP samples scored over both EP GFRP and EP ASGFRP samples in relation to percent water uptake content for different time periods as shown in Figure 5.21. Subsequently, Figure 5.22 illustrates the retention/percent change in mechanical properties for three GFRP compositions while, considering their respective unconditioned sample as the baseline for the calculation.

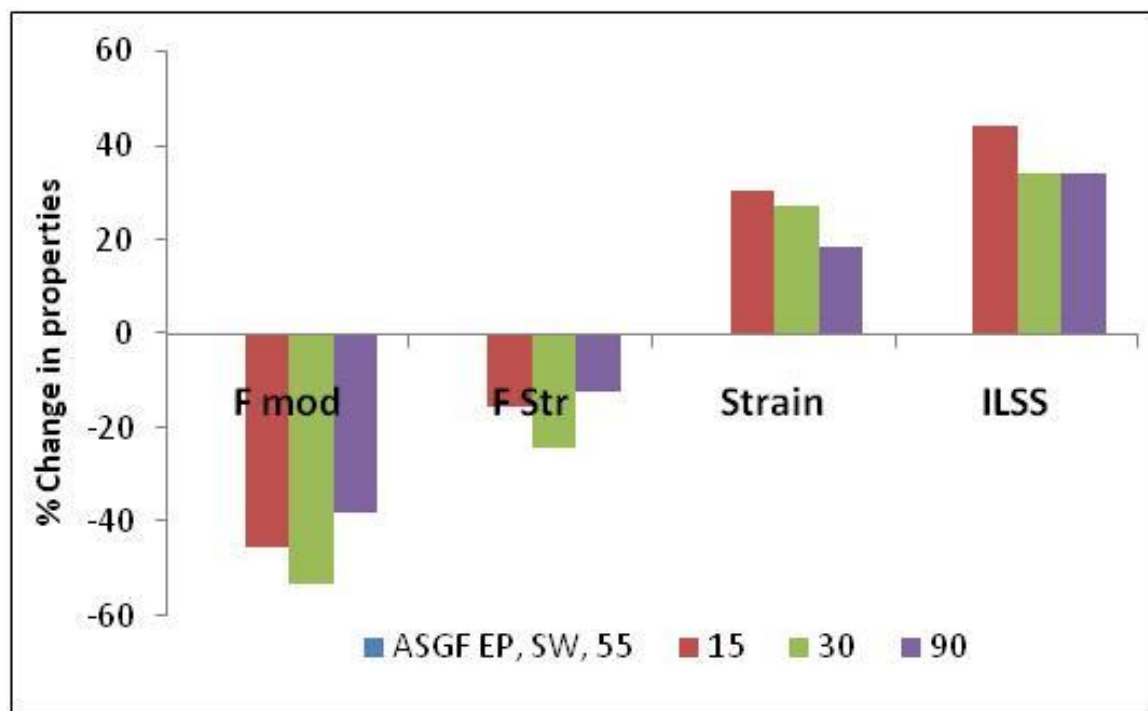
In general, the exposure of EP GFRP composites at an elevated temperature shows higher degradation for increased aging time. The exposure at warm environment acts as a catalyst and increases the rate of degradation of the composite material as compared to room temperature exposure. From the mechanical test results shown in Figures 5.22 (a, b and c) it was observed that the most effect on the flexural modulus was seen for EP ESGFRP samples. After prolonged aging, 90 days, in seawater at 55°C the stiffness of the EP ESGFRP composites decreased by 62% as interpreted from Figure 5.22a. Similarly, the reduction in flexural strength, strain at failure and ILSS properties signify the brittle failure, weakening of interfacial adhesion and debonding in the material with increased aging time. The degradation was a result of the formation of hydrogen bonds between the seawater molecules and silane groups present in the interface, thus causing a rupture of the interconnected network.

On the other hand, EP ASGFRP composites showed a different trend as compared to EP ESGFRP composites. Initially, there was a drop in stiffness and strength up to mid-time (30 days) but after that a recovery was seen as shown in Figure 5.22b. A possible reason that explains this behavior is the presence of excess amine molecules in the interface that contributes towards the excess water uptake and resin plasticization due to their strong hydrophilic nature. In addition to this, the thin layer of amino silane on the glass fibre surface protected them from serious damage by the seawater molecules. However, the fibre-matrix interface still got weakened due to excess water absorbed.

(a)



(b)



(c)

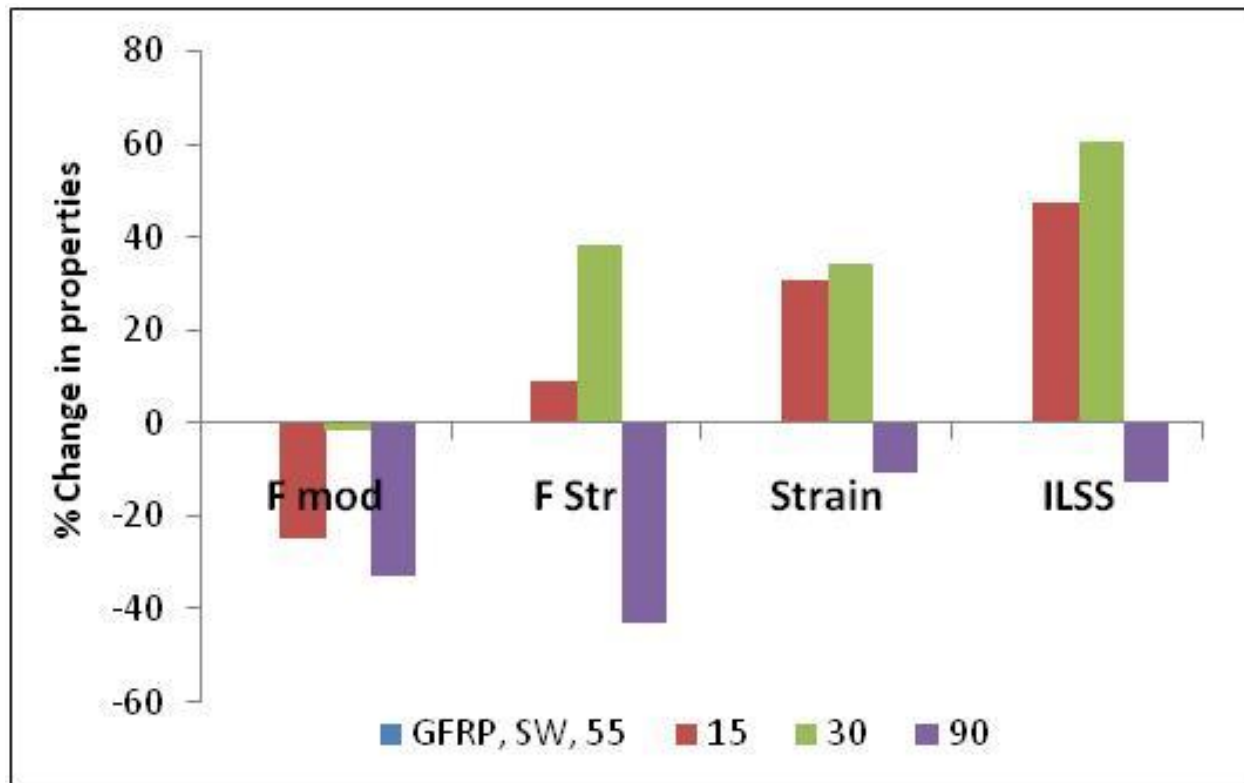


Figure 5.22: Percent change in mechanical properties after 15, 30 and 90 days aging in SW at 55°C for (a) EP ESGFRP; (b) EP ASGFRP; (c) EP GFRP composites

Similar behavior was also seen for the GFRP composites reinforced with amino-CNTs i.e. ACNT GFRP (as discussed earlier). Hence, it can be stated that the presence of additional amino groups in the composite has proven to be beneficial during hygrothermal conditions.

Lastly, the exposure of EP GFRP composites at an elevated temperature showed significant effect on the flexural properties as compared to ambient temperature. The experimental results were close to the expected behavior because at an elevated temperature the water molecules tend to cause more damage to the fibre-matrix interface and result in lowering the mechanical properties of composite materials. Also, in this composition there was the absence of matrix reinforcement and a thin silane layer on the fibre surface, which could try to protect them directly from harsh seawater when exposed at a higher temperature. Interestingly, the maximum percent weight gain was observed to be during the first month of immersion.

Additionally, the overall water uptake after three months of aging was also highest for the samples immersed at an elevated temperature (1.3%) versus room temperature (0.74%). This signifies that diffusion of water first entered the epoxy matrix, then into the fibres and finally reached the fibre-matrix interface. Interestingly, after one month of exposure the diffusion of water decreased significantly for EP GFRP specimens, but their effect on the mechanical properties was more severe as visualized by the sudden fall in mechanical properties (refer to Figure 5.22c). Figure 5.22c also illustrates a varying trend in flexural properties; with the best properties seen after 30 days of conditioning as was previously observed for EP GFRP samples aged at 25°C (refer to Figure 5.5). After about 30 days of exposure, the strain at break and ILSS appears to be reaching a plateau irrespective of the immersion temperature for EP GFRP samples. This plateau region was expected to be a temporary phase and would show a sudden drastic drop once the severe interfacial degradation and fibre stress corrosion took place thus, causing a major failure of the composite.

While, the significant fall in stiffness and strength of the material after one month conditioning can be explained by the slow aging mechanism, which states that, as the water travels toward the fibre-matrix interface it results in further delamination and debonding of fibres that indirectly affects its mechanical properties. Also, the hydrolysis of bisphenol A-epoxy resin by hot water is a form of chemical degradation of the matrix as the ester bonds are destroyed. As a result, it has a considerable effect on the mechanical performance of GFRP composites.

On comparing the mechanical performance of three different EP GFRP compositions, it is clear that the presence of excess amino groups in a composite tends to retain the mechanical properties even after prolonged aging at 25°C and 55°C. Thus, a comparison has been done between ACNT GFRP and EP ASGFRP composites samples immersed in SW to determine the composition that demonstrates better mechanical behavior with increasing aging time. For this purpose, the samples exposed at a higher temperature (55°C) have been chosen for comparison since; the material degradation was found to be much faster and higher vis-à-vis room temperature (25°C) for seawater conditions.

The summary of the results for both compositions has been listed in Tables 5.7 and 5.8.

Table 5.7: Mechanical behavior of ACNT GFRP samples after immersion in SW at 55°C

S. No.	Days	Samples immersed in SW at 55°C	Flexural Modulus (GPa)	Flexural Strength (MPa)	Strain at break (mm)	ILSS (MPa)	%M
1.	0	ACNT GFRP, SW	9.9	191	2.54	2.51	0
2.	15	ACNT GFRP, SW	4.6	120.5	3.5	3.17	0.76
3.	30	ACNT GFRP, SW	5.9	136	2.7	3.07	1.56
4.	90	ACNT GFRP, SW	7.5	145	2.65	3.05	3.19

Table 5.8: Mechanical behavior of EP ASGFRP samples after immersion in SW at 55°C

S. No.	Days	Samples immersed in SW at 55°C	Flexural Modulus (GPa)	Flexural Strength (MPa)	Strain at break (mm)	ILSS (MPa)	%M
1.	0	EP ASGFRP, SW	12.6	313.75	4.73	4.33	0
2.	15	EP ASGFRP, SW	6.9	266	6.17	6.25	1.39
3.	30	EP ASGFRP, SW	5.9	238	6.03	5.81	1.85
4.	90	EP ASGFRP, SW	7.8	275	5.6	5.82	1.93

From the results it can be interpreted that the modulus of both composites decreases significantly within first 15 days of immersion. While, the EP ASGFRP samples continued to show a decreasing trend for the next 15 days, i.e. up to 30 days, but ACNT GFRP samples immediately showed recovery in flexural modulus up to 90 days of immersion time. However, at the end of three months EP ASGFRP samples recovered its stiffness and had an approximately same flexural modulus as ACNT GFRP sample. A similar trend has also been witnessed for flexural strength with increasing aging time for both the samples. At the end of three months conditioning, ACNT GFRP and EP ASGFRP samples had lost 24% and 12% of their flexural strength, respectively. On the other hand, as the water intake into the composites increased, it showed a positive effect on the strain at break and ILSS of the composites as compared to unconditioned samples. Both ACNT GFRP and EP ASGFRP samples showed more than 30% increase in strain at break within 15 days of immersion. This implies that the presence of water in the composite's material tends to improve its ductility and flexibility.

In addition, ILSS showed an enhancement of 26% and 44%, respectively, after 15 days of conditioning for ACNT GFRP and EP ASGFRP samples, respectively. Interestingly, the strain at break deteriorated with increased aging time for both the samples, whereas, ILSS properties approached a stable value after one month of immersion. This suggests a strong interfacial bonding between the matrix and the fibres which was possibly supported by the chemical reaction between Cl^- ions or Na^+ ions, from seawater, and the glass fibres or amino groups in an epoxy matrix, respectively. A possible chemical reaction between sodium ions and the epoxy matrix had previously been discussed in Section 5.4.2.1 (refer to Figure 5.6).

Lastly, from Tables 5.7 and 5.8 it is quite evident that water content continued to show an increasing trend for ACNT GFRP and EP ASGFRP samples versus immersion time with significantly higher content recorded for ACNT GFRP samples. Therefore, as per the experimental findings severe degradation of the mechanical properties was seen in ACNT GFRP samples vis-à-vis EP ASGFRP samples. From the above comparative analysis at an elevated temperature, it may be estimated that the exposure of EP ASGFRP samples at room temperature (25°C) will outperform as compared to ACNT GFRP composition.

Hence, from this study it can be concluded that diffusion of water is dependent primarily upon several factors: (i) the type of water, (ii) matrix composition, (iii) protective sizing layer on the surface of glass fibre, (iv) edge coating of the samples and lastly immersion time. These parameters further affect the rate of diffusivity which in-turn is related to the materials lifespan, durability, strength, and stiffness.

In brief, the hygrothermal aging results provide a strong evidence that the presence of a thin silane layer on glass fibre is more advantageous as compared to presence of amino-CNTs in an epoxy matrix. In addition to that, EP ASGFRP samples had also scored over EP ESGFRP samples under the same conditions. Thus, it is feasible to report that it is challenging for the diffused water molecules to break the strong bonds between silane treated glass fibre mat and the epoxy matrix. In conclusion, surface treatment of glass fibres has proven to be more beneficial as compared to the addition of amino-CNTs in the epoxy matrix at a low concentration.

5.5 Closing remarks

The diffusion and mechanical behavior of 3 different GFRP composites was examined after exposure to hygrothermal conditions (in seawater (SW) and distilled water (DW)) both at high and low temperatures. The kinetics of water diffusivity results revealed that the water absorption during the initial stages followed Fickian behavior, but with prolonged aging the results were not the same. An interesting observation was that the maximum or equilibrium water content and the diffusion coefficient values were smaller for ACNT GFRP composites vis-à-vis EP GFRP composites when exposed to same SW and DW environments. Thus, even though amino groups in ACNT will tend to bond with water molecules, the other effect of CNT nano-fillers making the diffusion path tortuous for the water molecules seems to be the controlling step. Also, material deterioration was significantly more for immersion in SW as compared to DW. It is likely due to leaching of alkali oxides from the glass fibre surface that results in an excess seawater intake into fibre-matrix interface. This consequently causes swelling of the matrix, weakening the interfacial bonding and thus expedites the crack growth that eventually results in degradation of its properties. Interestingly, a decrease in mechanical properties was observed initially for ACNT GFRP samples, however, at a later stage the trend reversed and a recovery in the mechanical properties was clearly seen. On the contrary, PCNT GFRP composites revealed a continuous decreasing trend in mechanical behavior versus aging. The consistent fall in

properties, highlight the weak interfacial bonding, which deteriorates as more and more water diffuses through the fibre-matrix interface. Furthermore, exposure of composites at an elevated temperature resulted in quantitatively higher water uptake content accompanied by a steep fall in strength, stiffness and elongation-at-break of the composite. Lastly, exposure of silane treated EP GFRP composites in SW showed better mechanical response for amino silane glass fibre composites even after 90 days immersion period. Thus, highlighting the fact that a thin protective shield (from silane treatment) on the glass fibre surface shows overall better performance as compared to CNT GFRP specimens.

Chapter 6. Damage monitoring in GFRP laminates

6.1 Introduction

The focus of the research so far was to investigate the effect of EP GFRP modified by CNT and characterize the same by mechanical tests which are destructive in nature. It was also seen that exposure to mechanical tests and hygrothermal aging introduced defects/damages in the composites such as debonding, delamination, matrix cracking. It was interesting to note that few non-destructive methods had been applied in the past to locate these defects and quantify their severity in the FRP composites. However, from the literature, it was found that ultrasonic guided waves had emerged as an effective health monitoring tool for damage detection. Guided waves exploit the geometrical boundary (e.g. tube, cylinder or plates, etc.) of the structure as a guiding surface for wave propagation. In the structures with a plate or sheet geometry, guided waves are called Lamb waves. These are complex vibrational waves that propagate parallel to the surface throughout the thickness, thus scanning the entire thickness of the plate.

Nowadays, since the GFRP composites are replacing conventional steel/aluminum (or their alloys) for naval structures, it is imperative to develop their real-time health monitoring methodology in a submerged state using an advanced technique which could replace the conventional methods of testing. The present study is an attempt to ultrasonically monitor defects encountered in GFRP laminates using a non-contact, mobile and real-time guided wave technique. The main objective of this research was to develop a novel, non-destructive, *in-situ* and real-time experimental method for quick detection of manufacturing and in-service defects in GFRP laminates by using a pair of transducers in pitch-catch orientation, specifically used for underwater applications. Specific Lamb wave modes were generated by exploiting the submerged state of FRPs, wherein water was used as a natural couplant.

Lamb waves are usually excited by impinging the plate obliquely with an ultrasonic signal emitted by a high frequency transducer. As a result, variety of different waves are produced on excitation inside the material, which is followed by the superposition of longitudinal and shear waves in a thin plate with an infinite number of modes for both symmetric and anti-symmetric displacements within the layer. The wave propagation characteristics vary with the

incident angle, excitation and structural geometry. For the damage detection in FRPs such as cracks, delamination, missing fibre etc., a mode specific to the aforementioned defects needs to be excited. Desired Lamb wave mode in pitch-catch orientation can be selectively excited by arranging the transducers at a specific angle with respect to the specimen plate geometry. The incident angle, ' θ ', necessary to produce a desired Lamb wave which can be calculated from Snell's law as given in Equation (6.1):

$$\theta = \sin^{-1} \left(\frac{V_L}{V_{Ph}} \right) \quad (6.1)$$

where, V_L = longitudinal velocity of the incident wave in coupling media

V_{Ph} = phase velocity of desired Lamb wave mode

The preferred Lamb waves (other modes being suppressed) were experimentally determined by using normal beam transducers in a pitch-catch orientation.

6.2 Methodology

To develop a Lamb wave guided wave monitoring methodology, the first step was to generate different and specific guided Lamb wave modes by exploiting the submerged state of FRPs. The propagation characteristics of Lamb waves were investigated and studied by varying angles of the probes with the vertical (θ), distance travelled by the wave in water prior to its interaction with water (D_s) and Lamb wave propagation span through the specimen (P_s). After carefully selecting an optimum guided Lamb wave mode with strong signal fidelity in EP GFRP laminates, ultrasonic signals were recorded for healthy laminates. Further, these typical modes were used for comprehensive inspection of various types of manufacturing defects like air gaps and missing epoxy, introduced during preparation of EP GFRP laminates. Besides this, the service induced damages like notches and surface defects were also investigated and evaluated using guided waves by comparing the corresponding signal strengths. The developed methodology was then successfully implemented for structural health monitoring of hygrothermally conditioned specimens in seawater at different aging durations. The ultrasonic signal strength was related to the tensile strength of the conditioned EP GFRP laminates at different stages of aging to establish a correlation between destructive and non-destructive

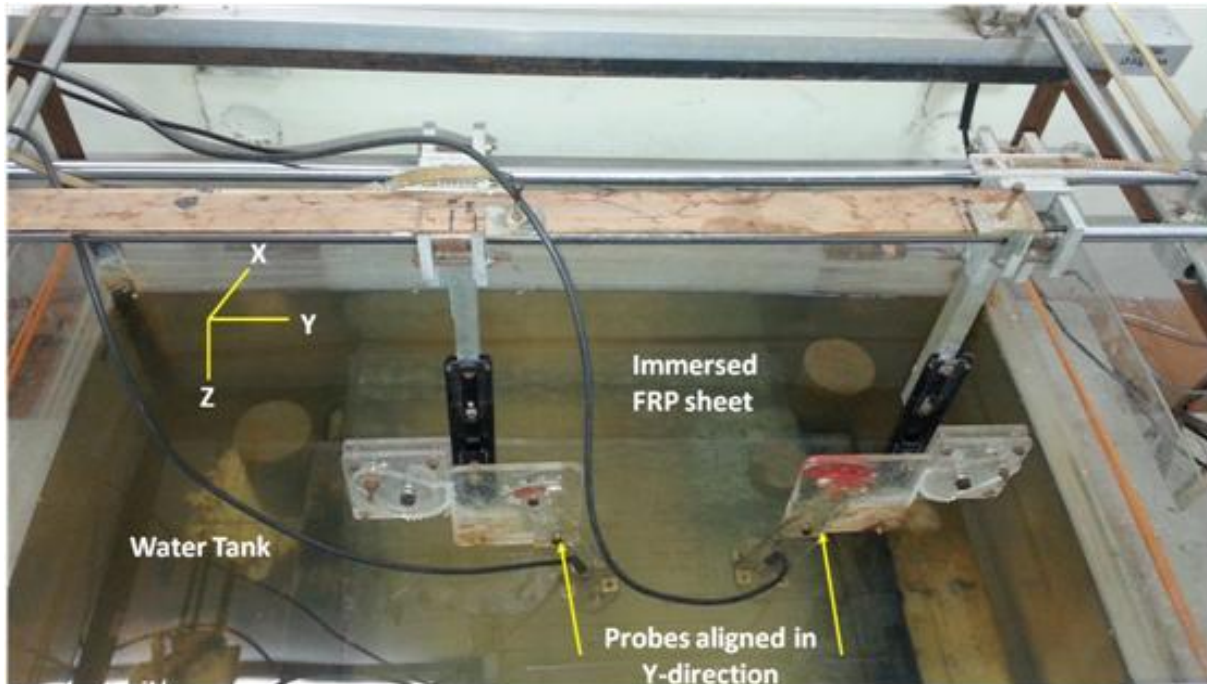
guided wave parameters to facilitate non-destructive evaluation of GFRP composites as a future scope of work.

The experimental set-up for the proposed damage monitoring technique has been discussed in detail in the sections ahead.

6.3 Set-up and specimen details

Experimental set-up comprised of an acrylic tank of dimensions (1500 mm x 1000 mm x 900 mm) filled with water to a depth of 700 mm. GFRP specimen fabricated by VARIM technique was fully immersed in water and placed in duly supported position. Figures 6.1 (a)-(b) show the actual and the schematic arrangement of the experimental set-up. Two holders designed to hold normal beam transducers, were assembled on top of the tank. Pair of transducers were placed in a pitch-catch orientation. This set-up exhibited four degrees of freedom (X,Y, Z, θ) over the submerged specimen as shown in Figure 6.1(a).

(a)



(b)

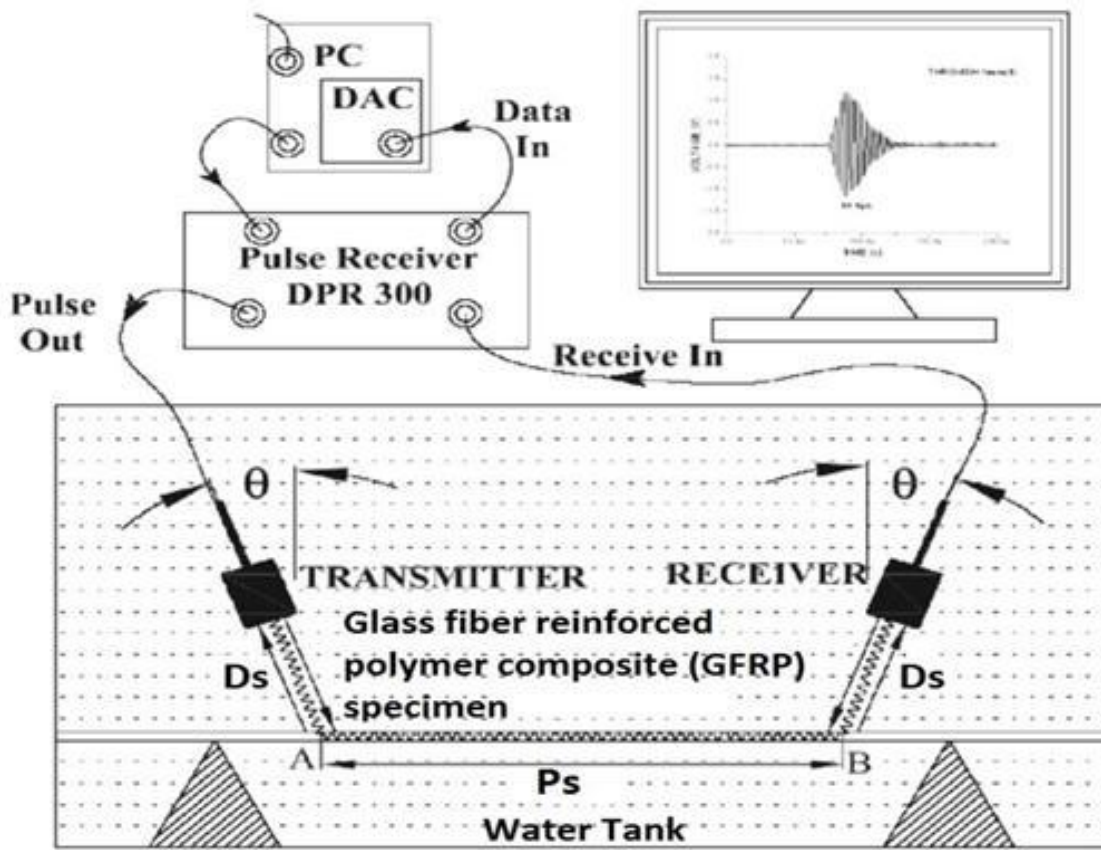


Figure 6.1: Experimental set-up (a) Actual; (b) Schematic arrangement

For ultrasonic investigations, an ultrasonic transmission (UT) system consisting of a Pulser-Receiver (PR) device (JSR make, Model DPR 300), ultrasonic transducers (Panametrics™ Immersion Probes) (as shown in Figure 6.2), data acquisition system (Agilent make) and display devices were used. Pair of immersion probes (Model No. A301S, Olympus Panametrics NDT) with a central frequency of 0.5 MHz were used in the present study. Figure 6.3 demonstrates the settings made on the JSR pulse generator in order to excite specific Lamb waves for GFRP sheet. The specific leaky Lamb waves were generated in the EP GFRP specimens by using pitch-catch arrangement as shown in Figure 6.1b. A lower frequency ultrasonic transducer is preferred for damage evaluation in thin FRP plates due to lesser material attenuation, scattering and mode conversions at lower frequencies as compared to higher frequencies.



Figure 6.2: Ultrasonic testing set-up

Probes were arranged at the same angle with vertical (θ) in order to make the receiver transducer more sensitive to the wavelength of input frequency while subduing noises (Figure 6.1b). The longitudinal waves generated by the transmitter probe travel through the surrounding water and impinge obliquely the surface of the laminate sheet. Desired Lamb wave mode can be generated by varying the angle of incidence (θ).

Another experimental parameter is the distance of separation (D_s) of probe and submerged sheet as shown in Figure 6.1(b). It is the distance travelled by the guided wave prior to its interaction with the submerged specimen. In this study, distance of separation was adjusted in terms of time of flight of longitudinal waves in water (t_s) in Pulse Echo (PE) mode. Both the transducers were placed with same D_s using PE signatures. This set-up was used for generating Lamb waves in Pulse Transmission (PT) configuration wherein longitudinal wave front generated by transmitter interacts obliquely with the specimen and receiver probe detects the propagating leaky Lamb waves through a fluid coupling on the other end. The distance of Lamb wave propagation through the specimen is termed as propagation span (P_s) as shown in Figure 6.1(b).

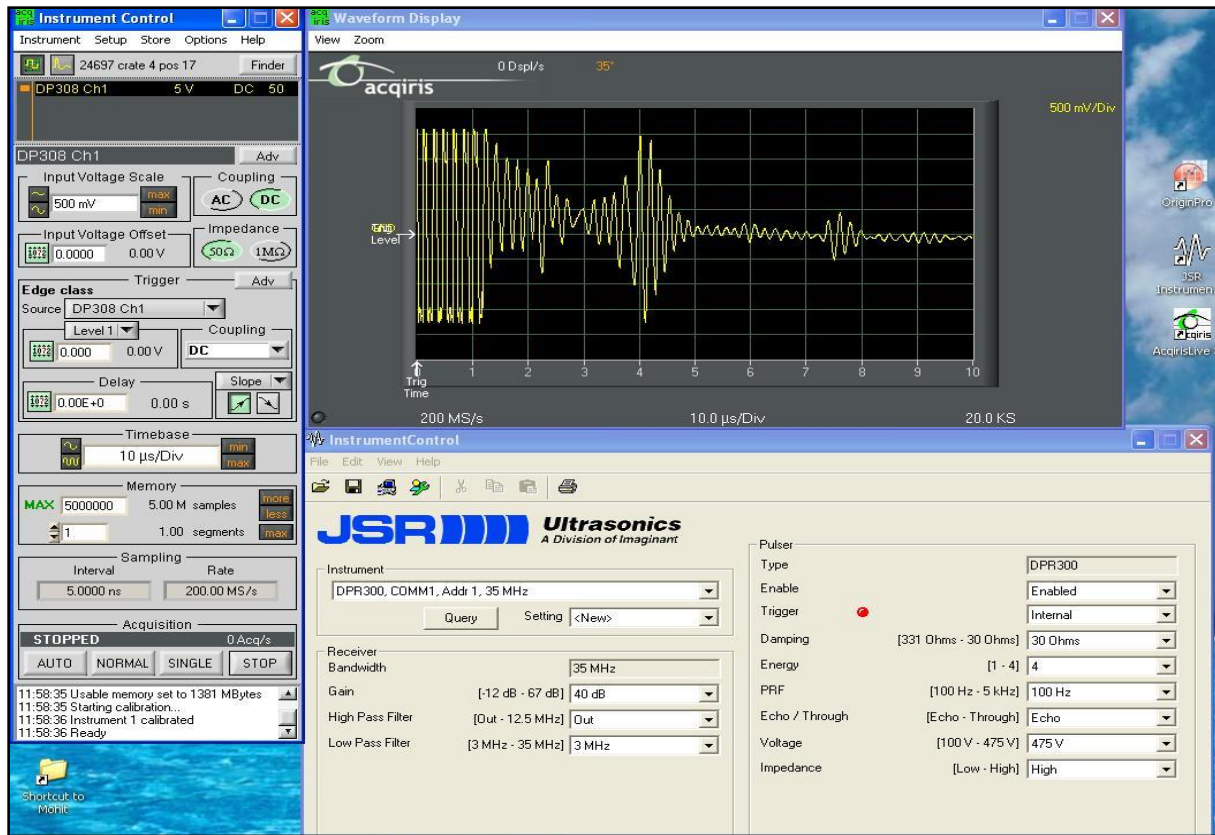


Figure 6.3: Configuration of JSR Pulse Generator

The literature reveals that Lamb waves exhibit multimode behavior in GFRP composites. It is therefore essential to obtain the desired Lamb wave propagation through the specimens with corresponding strong ultrasonic signal. For that purpose, choosing an optimum mode for testing depended upon the three main factors as stated above. Subsequently, healthy ultrasonic signatures with good signal fidelity were recorded initially for all the specimens which were then compared after moving the transducers over the defective regions in the sheet. Additionally, the effect of hygrothermal aging of the specimens was studied by comparing with healthy voltage amplitudes with specimens undergoing aging.

Figure 6.4 summarizes the various methodologies adopted to quantitatively and qualitatively evaluate the performance of CNT GFRP composites under different conditions.

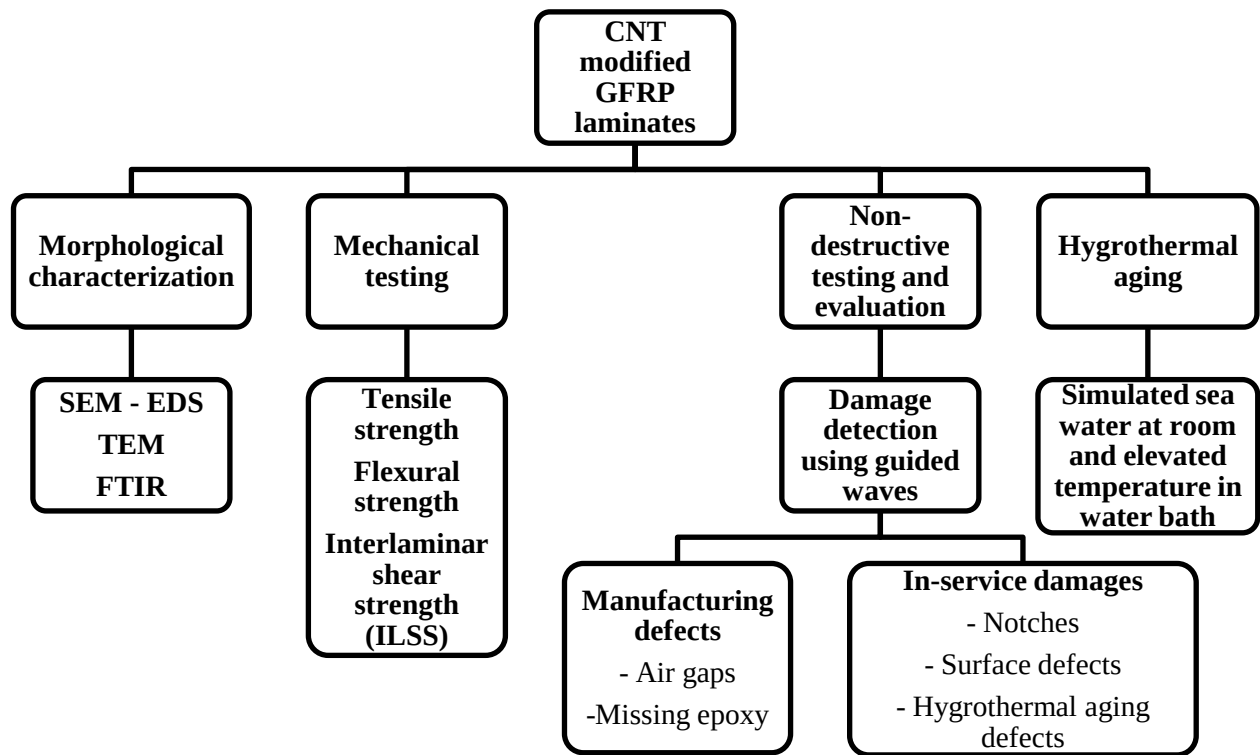


Figure 6.4: Quantitative and qualitative performance evaluation carried out on prepared CNT modified GFRP laminates

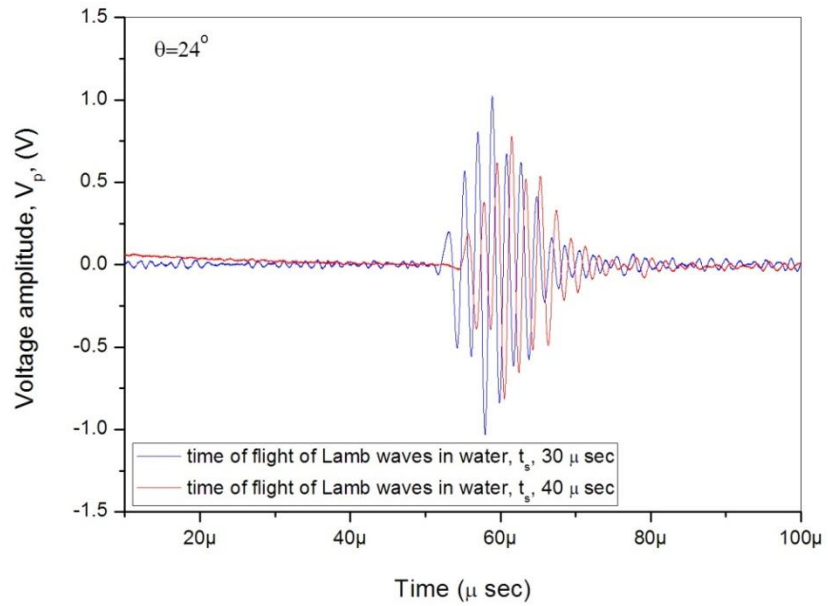
6.4 Generation of specific leaky Lamb waves in EP GFRP laminate

In-order to develop an effective monitoring strategy for EP GFRP laminate, good signal fidelity is a must. It was observed experimentally that large D_s resulted in excess loss of incident energy to the surrounding water and yielded a weak UT signal in PT mode. Also, too small a value of D_s resulted in field reflections that tend to superimpose over the initial ultrasonic signal. Thus, a suitable D_s and corresponding t_s for use in subsequent experiment had to be chosen.

6.4.1 Selection of optimum distance of separation (D_s)

Figure 6.5(a) shows the received signal amplitudes (V_p) obtained by using t_s of 30 μs and 40 μs while keeping other experimental parameters like P_s , θ and PR settings same. The trend of V_p with varying t_s (Figure 6.5b) clearly shows that V_p is approximately 20% greater when t_s is set at 30 μs as compared to 40 μs . Hence, for the subsequent experimental investigations both the probes were set at t_s of 30 μs .

(a)



(b)

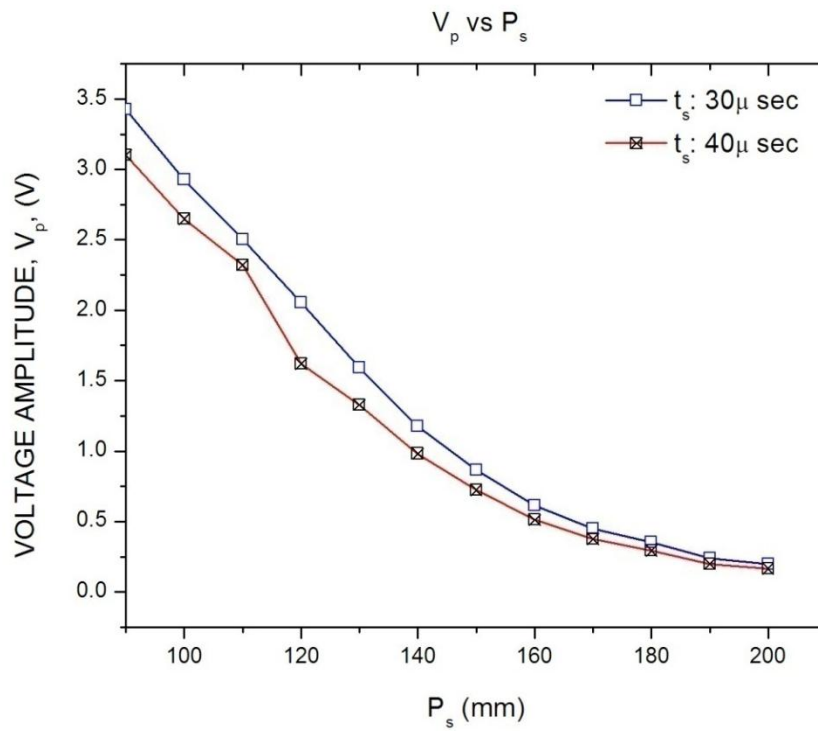


Figure 6.5: Effect of time of flight of guided wave in water medium (a) Specimen PT signature; (b) Trends of transmitted voltage amplitudes with varying propagation span for $\theta = 24^\circ$

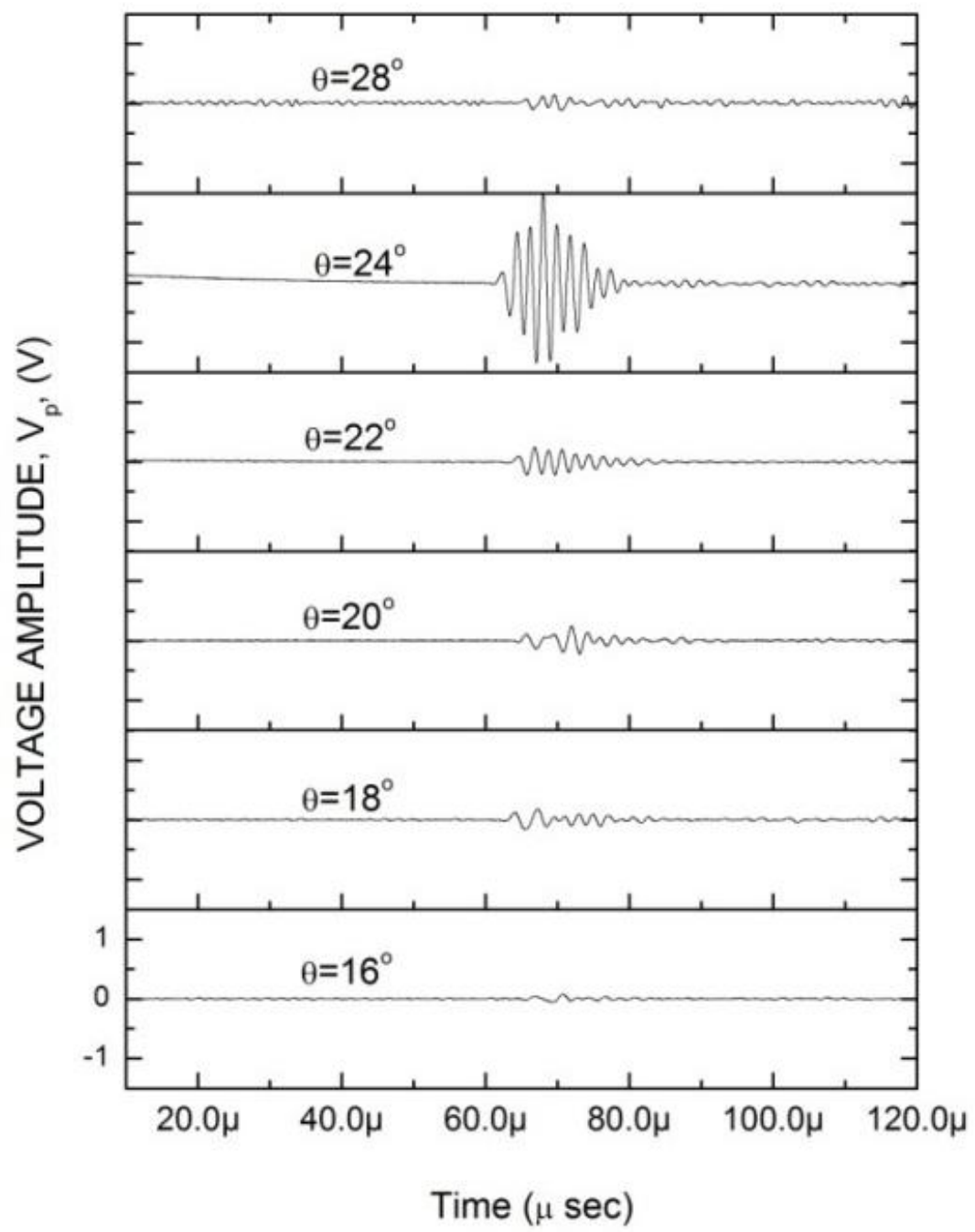
6.4.2 Selection of optimum angle (θ)

It is known that Lamb waves exhibit multi-mode behavior wherein each mode has a unique way of interaction with the defects in the specimen. Various researchers [Liu *et al.* 2001, Hay and Rose 2002, Sharma and Mukherjee 2010, 2011, Pistone and Rizzo 2013, Sharma and Mukherjee 2014, 2015a,b] have experimentally determined specific guided wave modes for effective health monitoring in pipes, rods, plates etc. In the present study, feasibility of generating Lamb wave modes in submerged EP GFRP sheets has been experimentally explored by varying the incident angle (θ) of the transducers in PT configuration. During the study, it was essential that the Lamb wave mode must exhibit distinct and sharp waveform with good signal fidelity and repeatability, so that after its interaction with the damage it may result in noticeable fall in signal amplitude.

Considering that, both the probes were placed with equal inclination (θ) and D_s with respect to the submerged EP GFRP laminate. During this study, P_s was kept as 100 mm for all values of θ . PT signatures were recorded by varying θ in steps of 2° starting with 0° as shown in Figure 6.6(a). On the other hand, Figure 6.6(b) shows the variation of received signal voltage amplitudes (V_p) with varying θ . No signal was detected by the receiver probe when θ varied from 0° to 10° . With further increase in θ (10° - 16°), traces of ultrasonic signals were observed in PT signatures. Distinctive signals with sharp peak were observed when θ varied from 18° to 24° (Figure 6.6a). However, with further increase in θ , the voltage amplitude reduced sharply, and no signal could be observed at higher values of (i.e. beyond 32°). This may be attributed to total reflection of the incident energy into the surrounding water.

Thus, Figures 6.6 (a)-(b) suggest that the inclination of the probes of 24° to vertical yields a UT signal with good fidelity that can be exploited for effective health monitoring purposes.

(a)



(b)

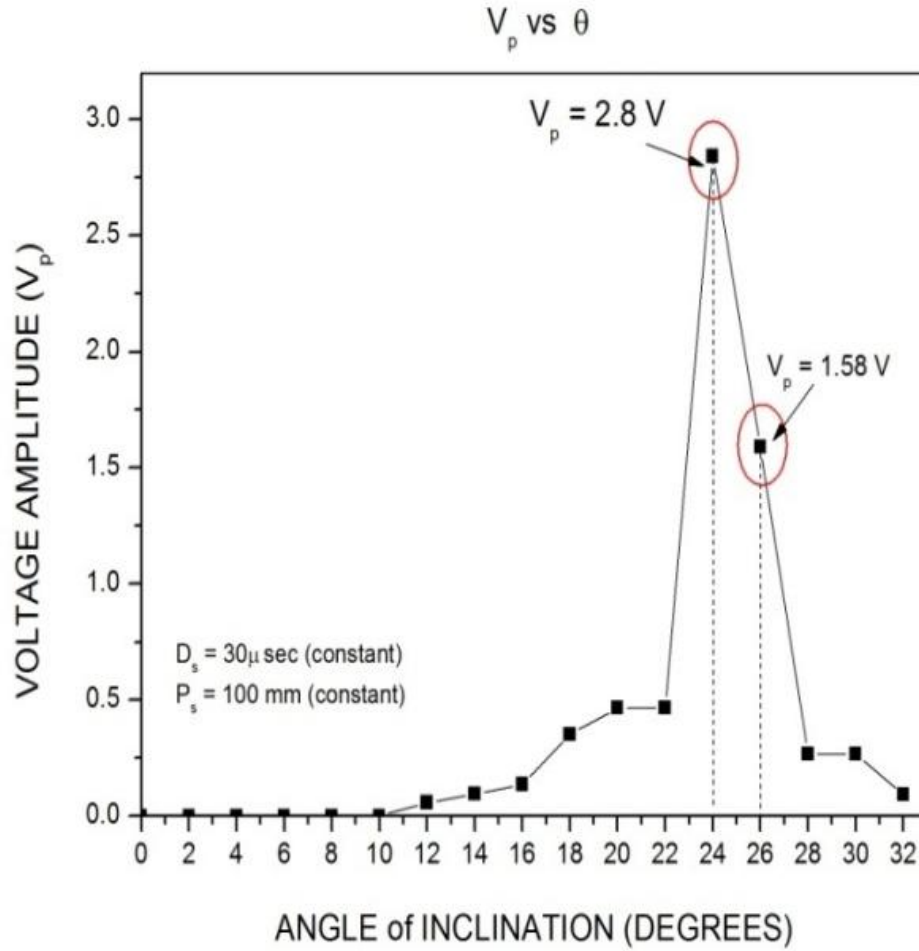
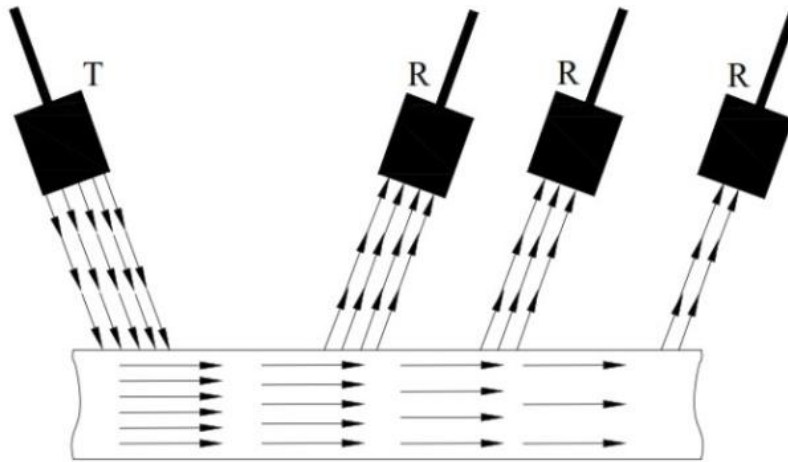


Figure 6.6: (a) PT signatures at different angles of incidence; (b) Trends of V_p (0° - 32°)

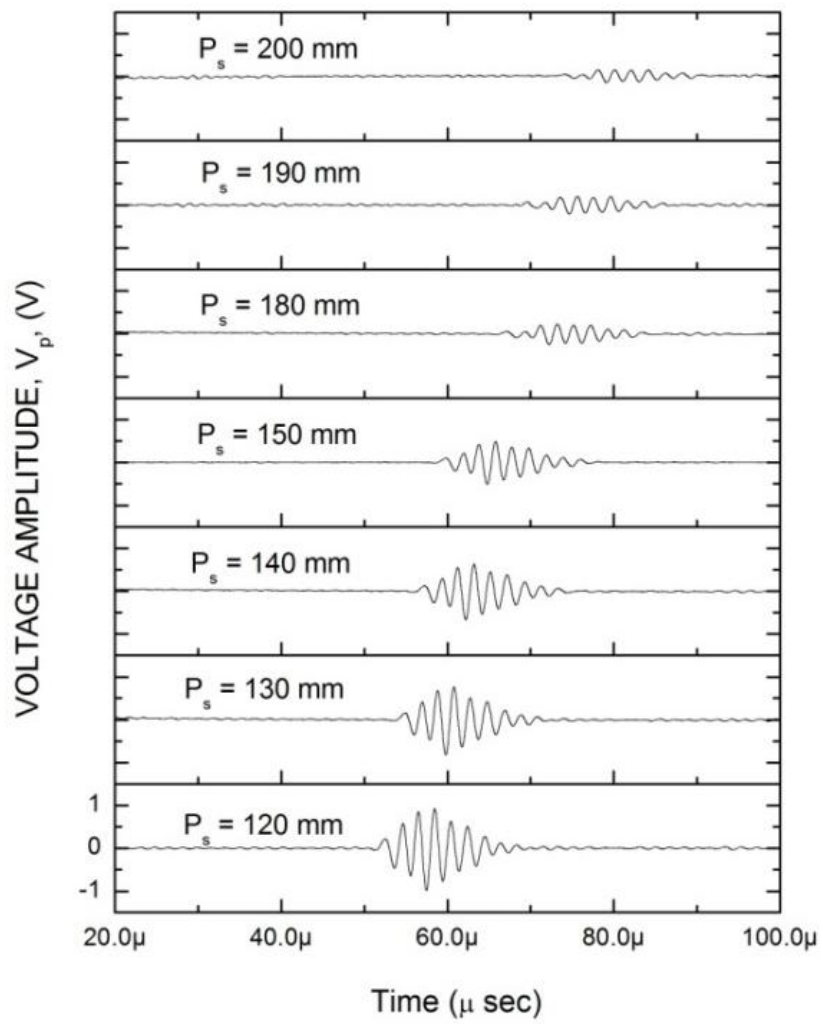
6.4.3 Selection of optimum propagation span (P_s)

The amplitude of signal for a given θ and D_s value is dependent upon the span travelled by the guided wave (P_s) through the submerged GFRP specimen. As the Lamb waves travels through submerged specimen, it loses energy continuously to the surrounding water, resulting in fall of signal strength as shown in Figures 6.7 (a)-(b). Longer propagation span shall lead to weak signal amplitude whereas; shorter spans shall result in longer inspection times for a given specimen. So it was important to choose a suitable P_s so that signal fidelity and inspection time could be optimally balanced.

(a)



(b)



(c)

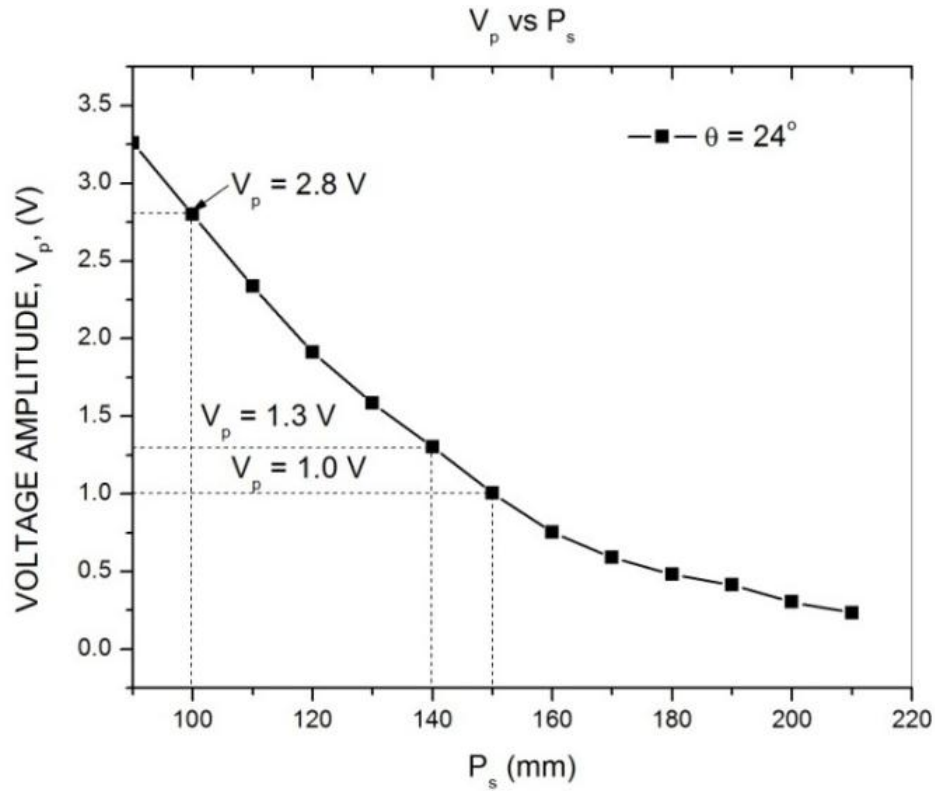


Figure 6.7: (a) Pulse transmission loss over propagation span length; (b) Effect on PT signatures by varying propagation span; (c) Trends of transmitted pulses with increasing span

Figures 6.7 (b)-(c) shows the variation of received signal strengths with varying P_s , while keeping other experimental parameters ($\theta = 24^\circ$, $t_s = 30 \mu s$) fixed. Figure 6.7(b) shows PT signatures for P_s in the range of 120 – 200 mm. Received signal showed good signal fidelity that was further utilized for effective health monitoring of EP GFRP laminates.

In Figure 6.7(c), value of V_p (2.8 V) at $P_s = 100$ mm is found to be consistent with V_p (2.8 V) in Figure 6.6 at $\theta = 24^\circ$ thus, ensuring the repeatability of the experimental procedure. Figure 6.7(c) suggests that propagation span (P_s) in the range of 100-150 mm, yields PT signals with V_p that can be exploited for health monitoring purposes at the given PR settings.

This study also provided another important wave propagation characteristic namely Group velocity (V_{gr}). As the P_s was increased from 90 mm to 210 mm in equal intervals of 10 mm, corresponding time of flight (TOF) of received signal was plotted. Figure 6.8 shows that

TOF varies linearly with respect to P_s . Group velocity of the propagating Lamb waves is given by inverse slope of this plot and calculated using Equation (6.2).

$$\frac{\Delta T}{\Delta D} (\text{Slope}) = 0.27923$$

$$V_{gr} = \frac{\Delta D}{\Delta T} = \frac{1}{\text{Slope}} = \frac{1}{0.27923} = 3.5813 \text{ m/sec} \quad (6.2)$$

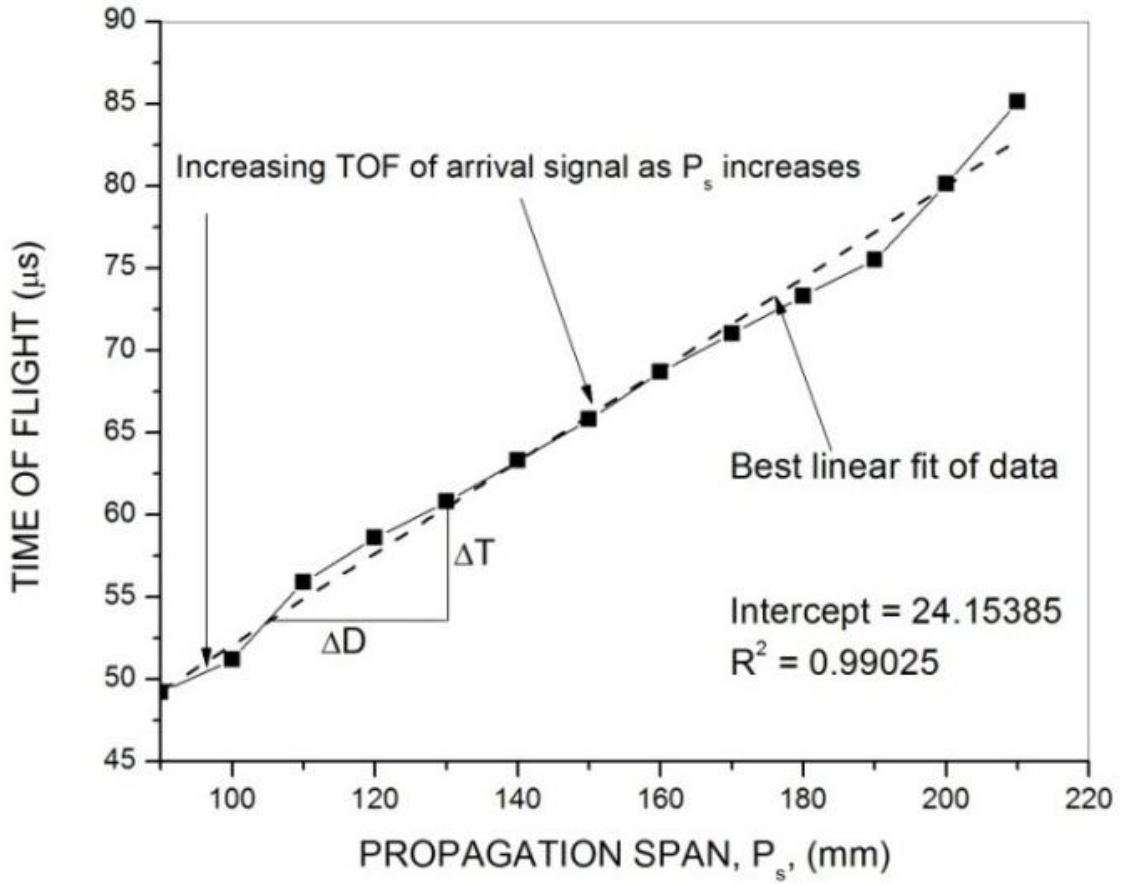


Figure 6.8: Time of flight versus propagation span at 24° in healthy region

V_{gr} can also be determined theoretically by inputting the values of t_s , T_t and P_s in Equation (6.3).

$$V_{gr} = \frac{P_s}{T_t - \left(\frac{t_{s,t} + t_{s,r}}{2} \right)} \quad (6.3)$$

where, P_s = propagation span between the transducers

T_t = Time of arrival of transmitted pulse in PT mode

$t_{s,t}$ = time of flight in water from transmitter (t)

$t_{s,r}$ = time of flight in water from receiver (r) probe

Figure 6.9 shows a recorded PT signature with P_s of 110 mm, $t_{s,t}$ and $t_{s,r}$ set at 30 μ s.

A single sharp peak appeared at $T_t = 58.6 \mu$ s as seen in Figure 6.9. Hence, the theoretically calculated group velocity of the Lamb waves is 3.84 m/sec which matches closely with that determined experimentally. The difference of 7% may be due to anisotropic behavior of the EP GFRP laminate and experimental inaccuracy in setting the exact incident angles.

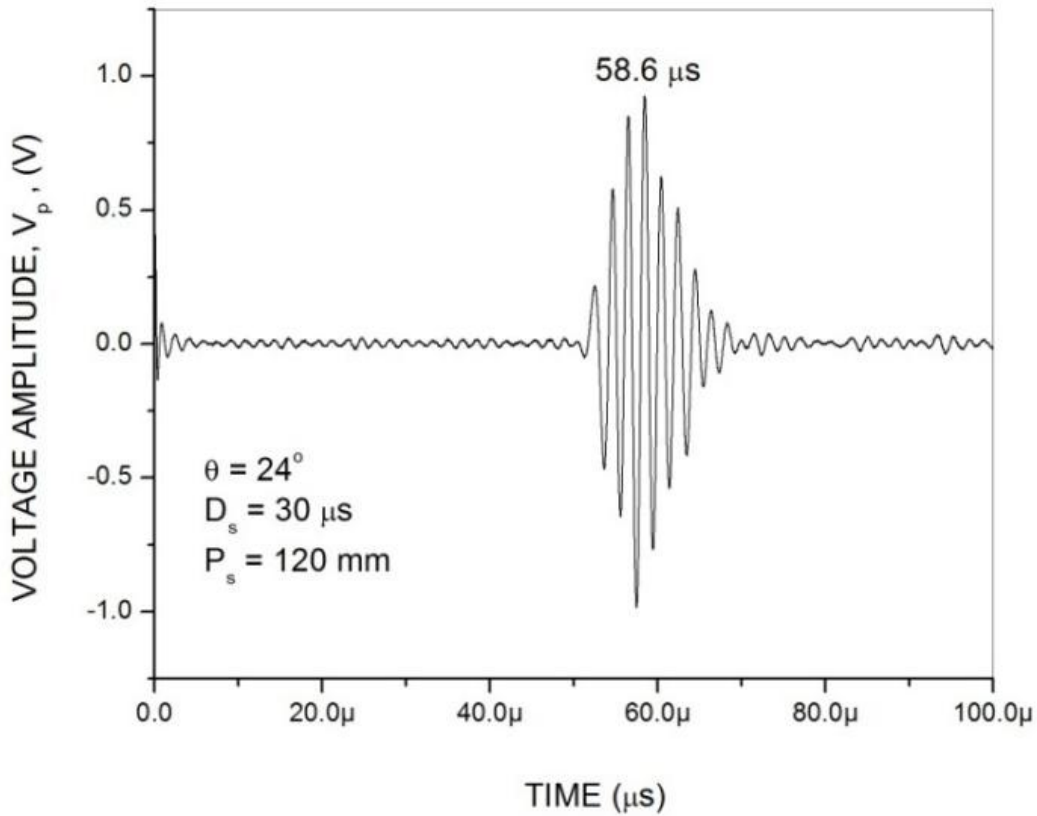


Figure 6.9: Sample PT signature to calculate group velocity theoretically

Equation 6.4 is used to calculate the phase velocity of Lamb waves in GFRP. This equation has been derived from the Snell's law equation as mentioned in Equation (6.1), where, the standard longitudinal velocity of wave in water is chosen i.e. 1.5 km/s and similarly, the experimentally determined critical angle value i.e. $\theta = 24^\circ$ is used.

$$\text{Phase Velocity} = \frac{1.5}{\sin^{-1}(24)} = 3.68 \text{ km/s} \quad (6.4)$$

The phase velocity and group velocity dispersion curves for the EP GFRP composites submerged in water seemed to be a complex mechanism to be modeled. However, sample phase velocity dispersion curves have previously been reported in the literature [Hayashi and Kawashima 2002, Hayashi *et al.* 2002, Hayashi and Rose 2003] by using a semi-analytical finite element method. It was stated that two fundamental modes propagate in the composite structure when using low frequency transducers up to 0.8 MHz.

A study by Hay [Hay *et al.* 2003] inspected the delaminated areas in composite skin-Nomex honeycomb specimens using ultrasonic guided waves. The sensitive mode was found experimentally by varying the frequency and phase velocity (in the range of 3500 – 4200 m/s) that effectively determined the delaminated zones in the composite structure. The experimental phase and group velocity results of the present study correlates well with those reported in literature. Therefore, the experimentally determined ultrasonic guided wave mode has been selected for the detection of manufacturing and usage defects in the composite laminates.

6.5 Defect detection using Guided waves

Broadly, there are two kinds of defects encountered in EP GFRP laminates – one which occurs during the preparation of GFRP sheet, i.e. air gaps and missing epoxy, and are termed as manufacturing defects and others which occur due to continual usage like notches/cracks, surface abrasion and are termed as usage defects or in-service damages. The interaction of specific guided wave modes with these defects is investigated further to facilitate development of damage monitoring methodology for laminates.

6.5.1 Manufacturing defects

During manufacturing, defects are likely to occur due to experimental inaccuracies or external factors. In the present study, defects in the form of air voids and missing epoxy were seeded while manufacturing the composite laminate. During the preparation of EP GFRP in VARIM, the vacuum pump was switched off for 30 min prior to the complete curing of epoxy resin, so that patches of voids in the form of air gaps were seeded in the fibre-matrix interface. Also, to introduce missing epoxy defects in the sheet, a layer of runner mesh on glass fibre mat

was removed at various locations resulting in resin deficit regions. A defect monitoring system using guided waves has been developed to detect these manufacturing and other service related damages in a composite sheet.

The nomenclature used for manufacturing defects and in-service damages in the EP GFRP composite sheet are listed in Table 6.1 and also shown in Figure 6.10.

Table 6.1 Nomenclature for manufacturing defects and in-service damages in EP GFRP composite sheet

Type of defect	Nomenclature	Details of defect type
Air voids	A1,A2,A3, A4	Air gaps
Missing epoxy	D1	Missing epoxy (normal to propagating wave)
	D2	Missing epoxy (oblique to propagating wave)
	D3	Missing epoxy (normal and oblique)
Notches	N1	25% depth, normal to propagating wave
	N2	50% depth, normal to propagating wave
	N3	25% depth, oblique to propagating wave
Surface defects	S1	Material removed parallel to propagating wave, dimensions of the defect: width = 4 cm and length 2 cm
	S2	Normal to the direction of wave and having dimensions: width 2 cm and length 3cm with more amount of material removed from the sheet as compared to S1.
	S3	Surface material was scratched obliquely to the propagating wave with dimensions: 2 mm width and 35 mm length
	S4	Surface material was scratched obliquely to the propagating wave and cut through GFRP sheet

6.5.1.1 Air gaps

The most important defect likely to occur in manufacturing of GFRPs is “porosity” – the presence of voids. They are typically caused due to small air molecules between the glass fibre layers, malfunctioning of vacuum pump or due to the air entrapped during processing of resin and hardener. The air gaps would result in minimal stress transfer from the matrix to fibres and is thus a critical parameter that needs to be detected. It affects the interlaminar shear strength (ILSS) and severely mars the structural performance of specimen. The voids in the GFRP are difficult to see with the naked eye, but become apparent when submerged in water.

For the given specimen, air gaps were marked on the sheet as shown in Figure 6.10. Various locations in the specimen illustrate the possibility of voids which are marked as A1- A4, and are also listed in Table 6.1. Ultrasonic pitch-catch testing was carried out in the identified zones in the sheet to study the effect of air gaps on the signal fidelity. For the testing purposes, both the probes were placed in pitch-catch arrangement at an angle of incidence of 24° and the signal was recorded at a propagation span of 110 mm and 120 mm. The presence and extent of air gaps in the composite can be estimated ultrasonically by comparing the PT signal amplitude at the defective locations vis-à-vis healthy signal amplitude. Initially, PT signatures were first recorded in the adjacent healthy region adjoining the air gaps and then the transducers were moved along X-Y axis to record the ultrasonic signal at marked air gap locations in the sheet. The voltage amplitude of the received signals was normalized with respect to healthy signals in order to avoid any bias.

6.5.1.2 Missing epoxy

Another common manufacturing defect observed in the EP GFRP sheets is the missing epoxy defect observed in poorly prepared composite sheets having patches of rich or deficient resin regions originating due to non-uniform spread of the polymer matrix. This defect can be identified by carefully observing the EP GFRP sheet and is indicated by an exposed glass fibre layer having no epoxy resin coating on it. Although, the resin is being infused into the mold through an efficient mechanism still, such defects occur during VARIM, possibly due to uneven mesh distribution (which assists the resin flow) or due to inhibition of resin flow by the inlet pipe, etc.

Missing epoxy defects induced during manufacturing of the sheet have been identified on the specimen as D1, D2, and D3 as shown in Figure 6.10. On moving the two probes along X-axis of the tank, the marked regions with missing epoxy defects were found to be either normal (D1) or inclined (D2), to the propagating Lamb waves (i.e. X-direction of the GFRP sheet). The PT signatures were recorded at the defective sites (D1 - D3) while keeping parameters such as θ , D_s , P_s and PR settings unchanged. For carrying out a comparative analysis on the same scale, the recorded voltage amplitudes were normalized with the healthy voltage amplitude for each missing epoxy location.

6.5.2 Usage defects (simulated)

Due to various environmental and loading factors, degradation of the composites (in-service) takes place, which needs to be monitored periodically in order to avoid catastrophic failures. The internal defect such as material degradation and fibre breakage in GFRPs may be attributed to numerous factors such as overloading, impact loads, fatigue, hygrothermal effects, over-heating, creep, etc. Also, the penetration of moisture and other small molecules could degrade the interfacial properties due to the plasticization effect on resin. Additionally, the external defects like cracks, abrasion, notches, scratches, etc. also affect the performance of GFRP. These damages manifest in the form of delamination and debonding of the specimen, which results in lowering the mechanical properties such as stiffness and strength of the composites. In the present study, usage defects have been simulated in the prepared composite sheet in the form of notches and surface defects.

6.5.2.1 Notches and surface defects

In this study, for both notch and surface defects, the effect of normal and oblique inclinations has been investigated by carrying out comparative analysis of their respective signal amplitudes with healthy signal. Initially, the PT signatures were recorded in the healthy region using the selected Lamb wave mode (at $\theta = 24^\circ$). Subsequently, a notch, N1, being 0.5 mm wide and with a depth of 25% of sheet thickness, normal to the Lamb waves (X-direction) was machined (Figure 6.10) for which the ultrasonic signatures were recorded. Further, the transducers were slightly moved along X-axis (of the tank) to record the ultrasonic signal for another notch, N2, having width same as N1, but, with an increased depth of 50% of the sheet

thickness. Besides this, a notch, N3, at 60° to the horizontal with 1.5 mm width and 25% thickness of the sheet was also machined (Figure 6.10) and PT signatures were recorded for the same.

Apart from the above mentioned notches, GFRP composites may also encounter surface defects called abrasions (like scratches, material degradation) during its service conditions which over longer time period significantly affect the strength and stiffness of the composites. The presence of surface defects in EP GFRPs were also monitored using the non-contact technique discussed in this study. Initially, the ultrasonic signals were recorded in the healthy region by exciting the selected Lamb wave mode travelling along X-direction (as labeled on submerged GFRP sheet). Subsequently, material losses due to surface abrasion or scratches were seeded on the specimen by scooping out the material using a cutter. These surface defects machined on the sheet have been identified as S1, S2, S3 and S4 (refer to surface defects in Figure 6.10).

The location S1 depicts a region parallel to the propagating wave (with dimensions: width = 4 cm and length = 2 cm) as compared to the S2, which is normal to the direction of the wave and has a larger amount of material removed from the sheet compared to S1 (with dimensions: width = 2 cm and length = 3 cm). Further surface defects at an obliquity were also marked on locations S3 and S4 both with the same dimensions (i.e. width = 2 mm and length = 35 mm) but having varied depths of 60% and 90%, respectively, were seeded at 60° (with respect to X-axis) in the EP GFRP sheet. UT signatures were similarly taken at healthy as well as S1- S4 locations.

In brief, for the experimental study and to ensure good signal fidelity and repeatability of results, the time of flight for the probes (in pitch-catch orientation) was set at 30 μ s in PE mode, θ at 24° and span length (P_s) of 110 mm and 120 mm was kept constant throughout the investigation. The PT signatures were initially recorded for healthy regions in the submerged GFRP sheet. Subsequently, by moving the transducers along X-axis, the signal produced during the interaction of Lamb waves, with damages and defective zones was recorded and compared vis-à-vis to healthy region.

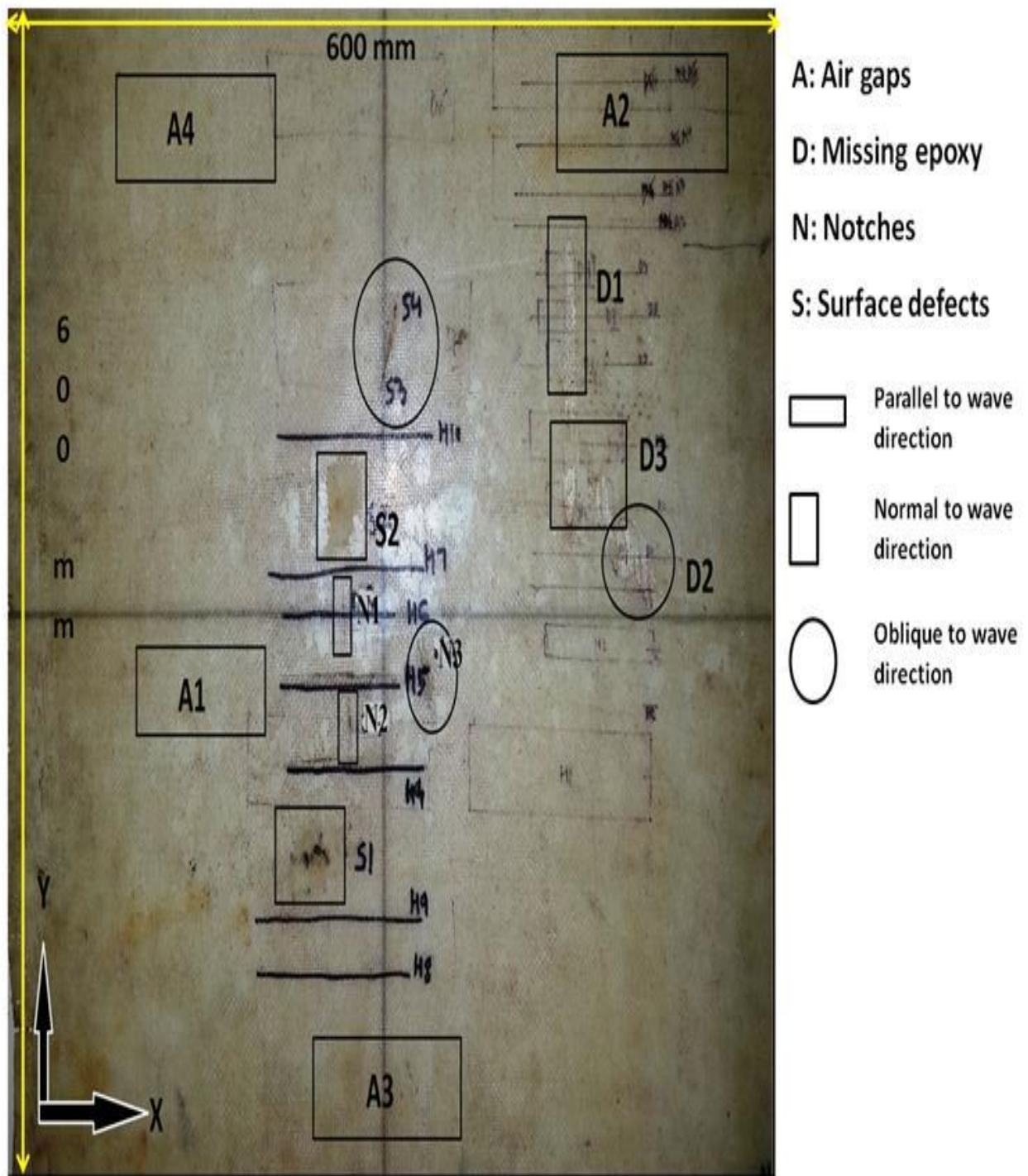


Figure 6.10: Photograph of actual EP GFRP sheet with manufacturing defects (air gaps and missing epoxy) and in-service damages (notches and surface defects)

6.6 Results and discussion

For the EP GFRP composites, during the propagation of Lamb waves, PT signatures are likely to be affected when they encounter any type of defect in the submerged specimen. Effect of manufacturing as well as usage defects in the EP GFRPs has been investigated and discussed in the following sections.

6.6.1 Presence of air gap

The air gets entrapped in the sheet either during the resin preparation or due to vacuum leakage during the fabrication, results in a significant decrease in interlaminar shear strength of composite. Air gaps in a composite sheet does not produce a discrete reflection, but scatters the ultrasonic wave in different directions, also resulting in transmission loss. The PT signatures and the V_n trends have been obtained for selected Lamb wave mode for healthy and varying lengths of air gap patches in the GFRP sheet. Figure 6.11 shows PT signatures recorded over the healthy region and air gap locations (A1-A4) in the submerged specimen.

The PT signature for the healthy and defected region highlights that after interaction with the air voids in the composite sheet, the signal remains unaltered and no mode conversion is observed. But a drop of 32% in the voltage amplitude is seen after interaction with A1 while, the shape of the arriving peak and TOF remains unaltered. Voids in the sheet tend to change the acoustic impedance and consequently less energy is transmitted to the receiving transducer which is indicated by a drop in the signal amplitude. Quantitative change in signal strength vis-à-vis voids in the EP GFRP specimen with respect to healthy signal is an indication of the extent of air gap.

The trend of V_n versus air gap locations (A1 – A4), seen in Figure 6.12, illustrates a decrease in the V_n of the recorded signal as the Lamb wave propagates through the air gaps compared to healthy region. Some locations have shown more drop in the received signal as compared to others which could possibly be due to the varying amount of air present in the fibre-matrix interface. The drop in signal strength vis-à-vis healthy signal is observed to be approximately 32%, 45%, 55% and 56%, at locations A1, A2, A3 and A4, respectively with $\theta=24^\circ$ and $P_s = 110$ mm. A similar trend has been witnessed by further increasing the span length (P_s) between the probes to 120 mm. Moreover, there is a linear decrease in V_n as the length of air

gap increases. Interestingly, for a similar length of air gap patches at locations A3 and A4, a negligible change in signal strength is witnessed which suggests the repeatability of the experimental results.

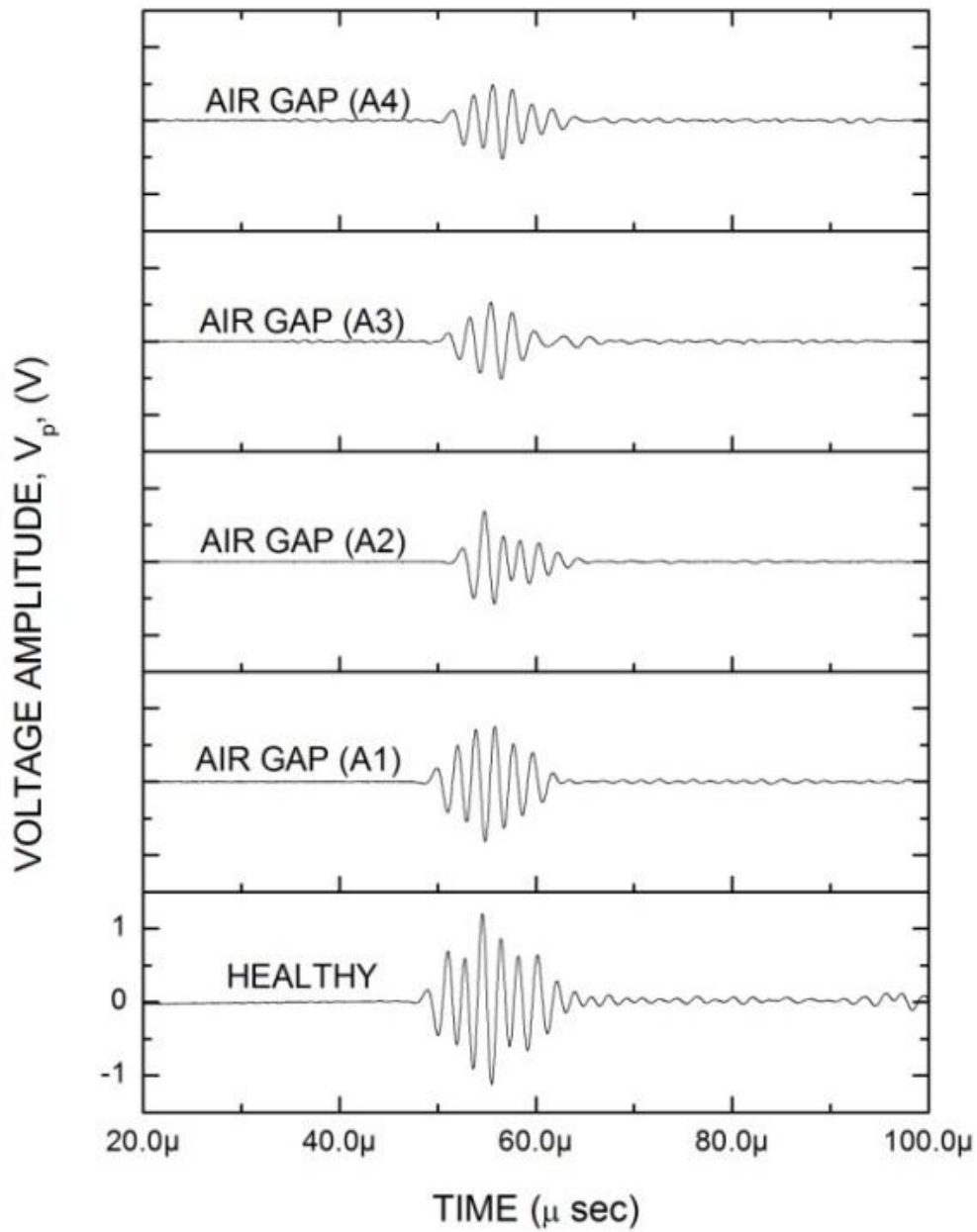


Figure 6.11: Effect on PT signatures with air gap locations (A1-A4) vis-à-vis healthy region

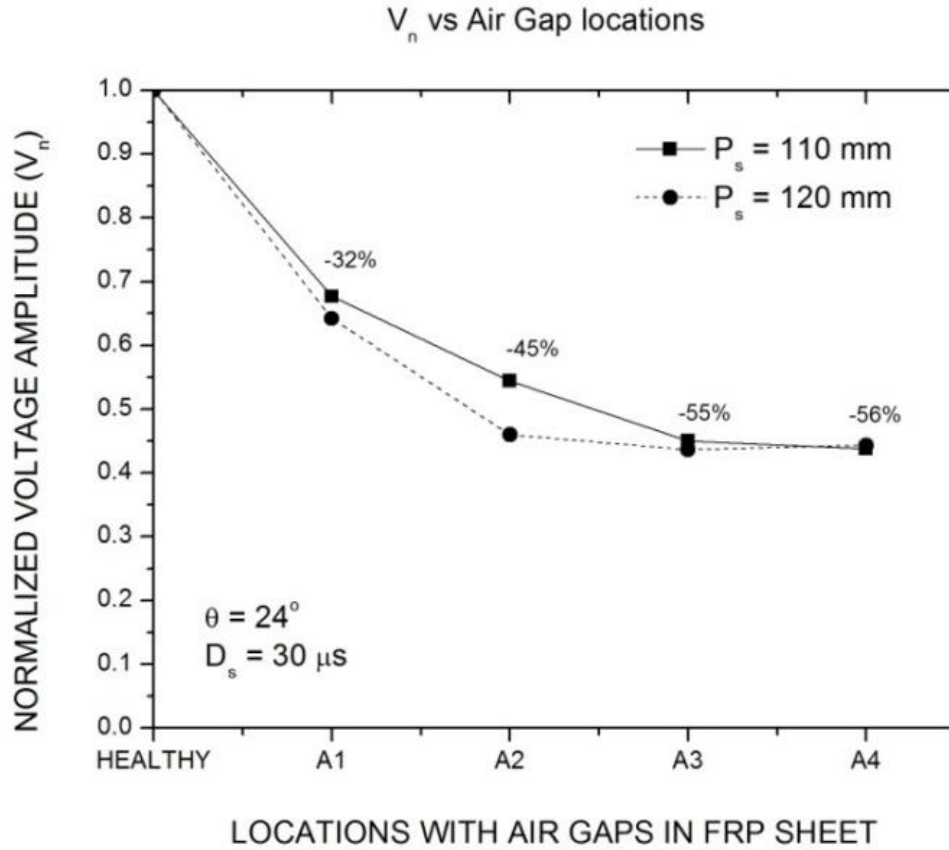


Figure 6.12: Trends of normalized transmitted pulse voltages with presence of air gaps

Hence, it is observed that as the length of air gap increases, V_n of the recorded signal diminishes. These variations highlight the efficacy of selected Lamb wave mode for detecting manufacturing defects like air voids in the fibre-matrix interface by drop in signal amplitudes as the waves interact with the air gaps.

6.6.2 Missing epoxy

The missing epoxy refers to the non-uniform distribution of resin over the fibre sheets. The effect on PT signature with missing epoxy locations (D1- D3) compared to healthy signal is shown in Figure 6.13. While, Figure 6.14 shows the decreasing trend observed in the UT signals with missing epoxy defect vis-à-vis healthy region in the composite sheet. It is observed that as the Lamb waves propagate in the regions with missing epoxy, voltage amplitude of the received signal diminishes. The missing epoxy regions were oriented in different directions, such as normal, oblique and both normal and oblique to the direction of Lamb waves (i.e. along X-

direction in sheet). Comparison of healthy region with respect to the missing epoxy defect in terms of normalized voltage amplitude indicates that the transmitted pulse amplitude varies with the direction of the defect.

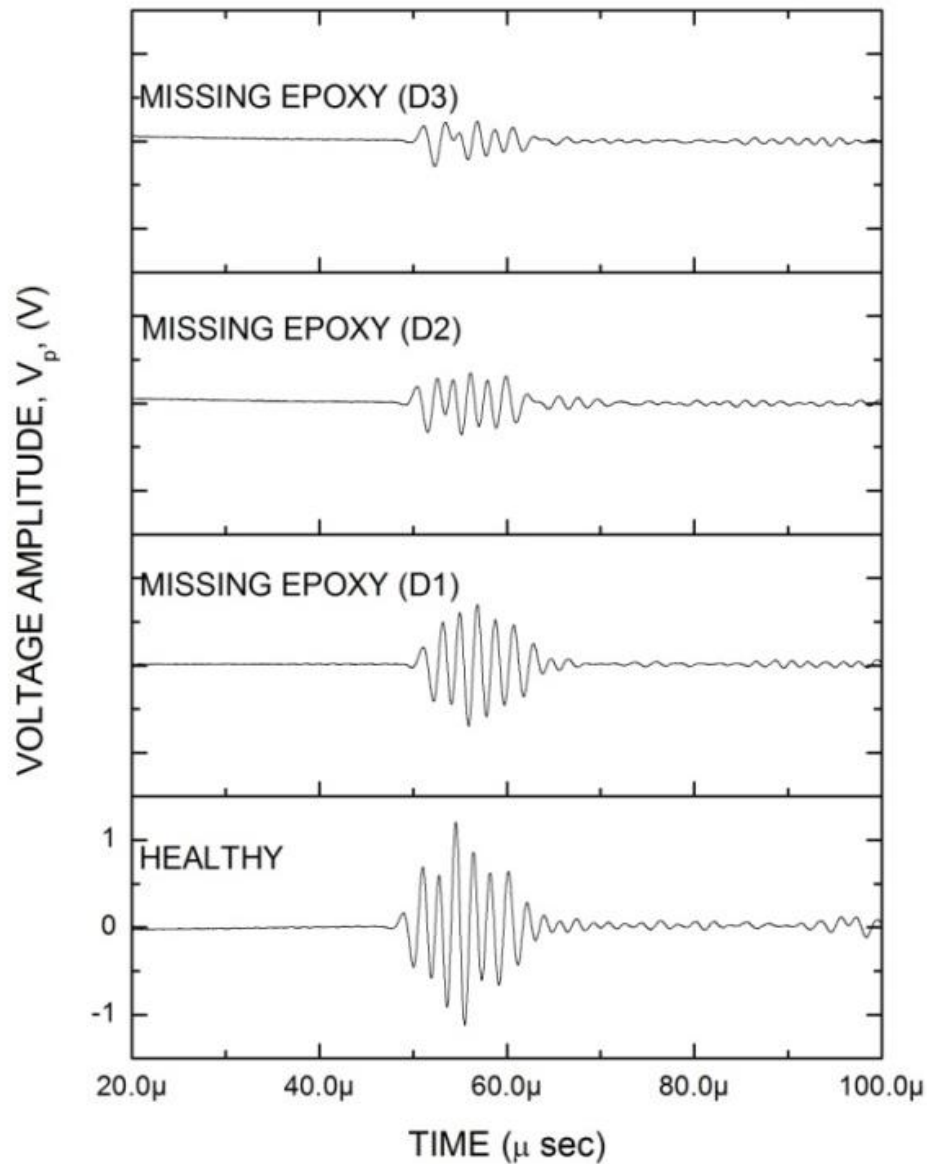


Figure 6.13: Effect on PT signatures with missing epoxy (D1-D3) vis-à-vis healthy signal

The initial fall in V_n for normal missing epoxy defect (D1) is 40% of the healthy voltage amplitude and is 70% for oblique epoxy defect (D2). This fall is considerably significant as compared to the fall in V_n experienced for location D3, consisting of both normal and oblique

defect. From Figure 6.14 it is clear that by changing the propagation span between the receiver and the transmitter there is no change in the type of signal recorded and a similar trend is followed for all the missing epoxy locations studied. The drop in V_n is steepest at D3 being 78% for P_s of 110 mm and increases to 81% for P_s of 120 mm as shown in Figure 6.14.

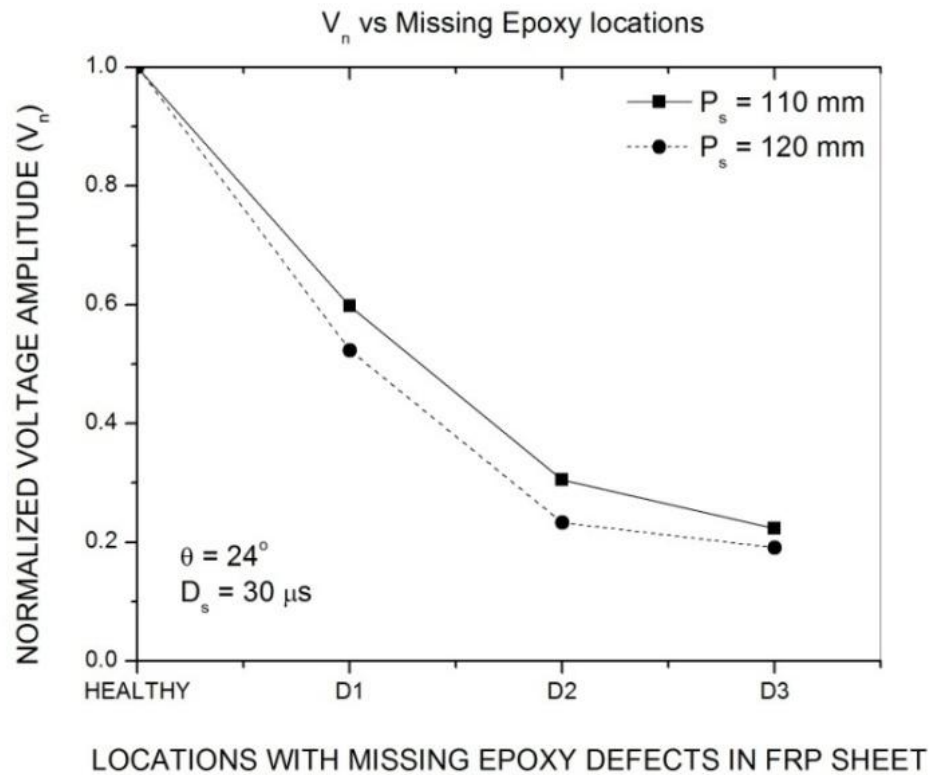


Figure 6.14: Trends of normalized transmitted pulse voltages with different missing epoxy defects

Ultrasonic Lamb waves are sensitive to manufacturing defects like air gaps and missing epoxy created during manufacturing of laminate and hence can be effectively used for identifying internal defects in the GFRP sheets immediately after they are manufactured and cured. This technique can go a long way in improving the quality of the composite laminates where they are put to use or applied. The developed non-contact and non-invasive Lamb wave technique can be effectively used for damage monitoring and quantifying the defects induced during manufacturing of GFRPs.

6.6.3 Notches and surface defects

In the prepared EP GFRP laminates, effect of increasing notch depth and orientation of notch on ultrasonic signal strength has been investigated with respect to healthy signal. Figure 6.15 shows the effect of machined notches of varying depths on the received UT signal amplitude vis-à-vis their respective healthy signals.

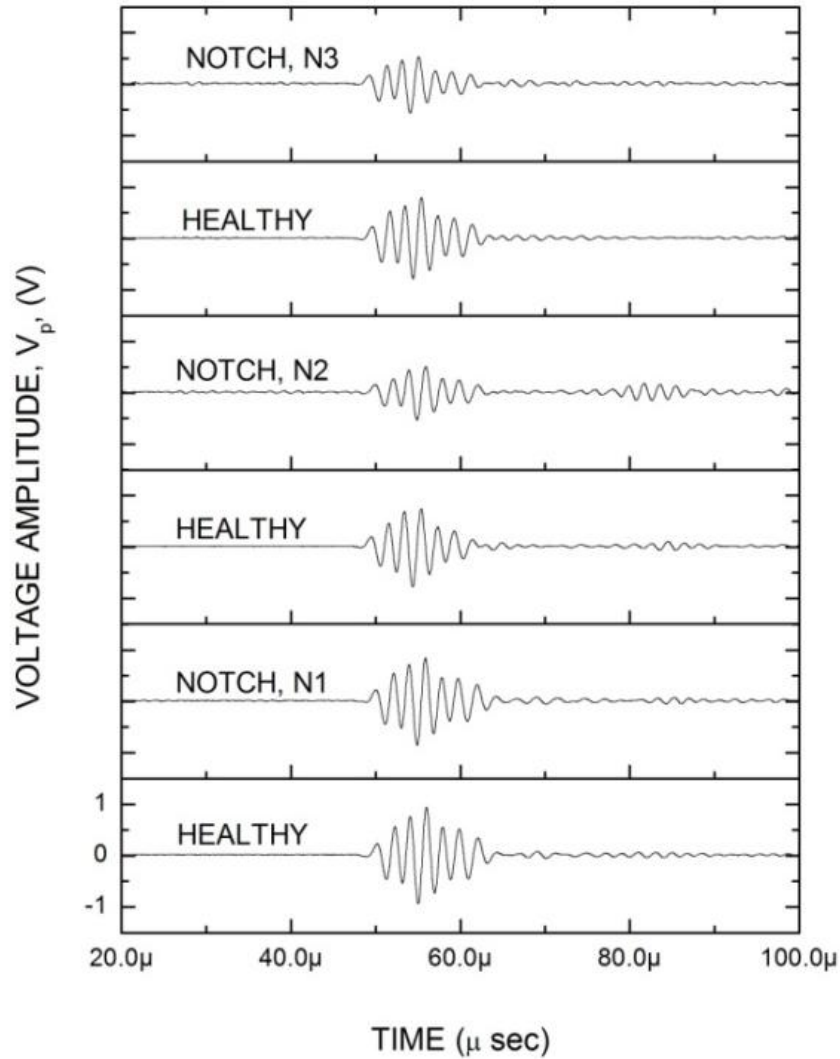


Figure 6.15: Effect on PT signatures with notches (N1-N3) vis-à-vis healthy signal

Figure 6.16 clearly illustrates that as the percentage depth of notch increases, voltage amplitude of UT signal decreases. It is possibly due to the increased reflection and scattering of the Lamb waves from the vertical wall of the notch.

The fall in voltage amplitude for 25% notch depth (N1) is 8.9% and is 31% for 50% notch depth (N2), as compared to their respective healthy regions. However, an inclined notch (N3) with the same depth as N1 i.e. 25%, shows 31% drop in V_n with respect to its healthy signal. Hence, significant drop in the received signal amplitude is observable as the depth and inclination of the notch increases. A similar trend is followed at $P_s = 120$ mm with a fall in voltage amplitude of 12%, 34% and 33% for N1, N2 and N3, respectively which establishes the repeatability of the experimental set-up. Hence, this technique gave a fall indication of the effect of notches on the amplitude of the signal transmitted. This establishes the efficacy of guided waves in identifying defects like internal cracks, or fatigue cracks in GFRP sheets simulated as notches in the present study.

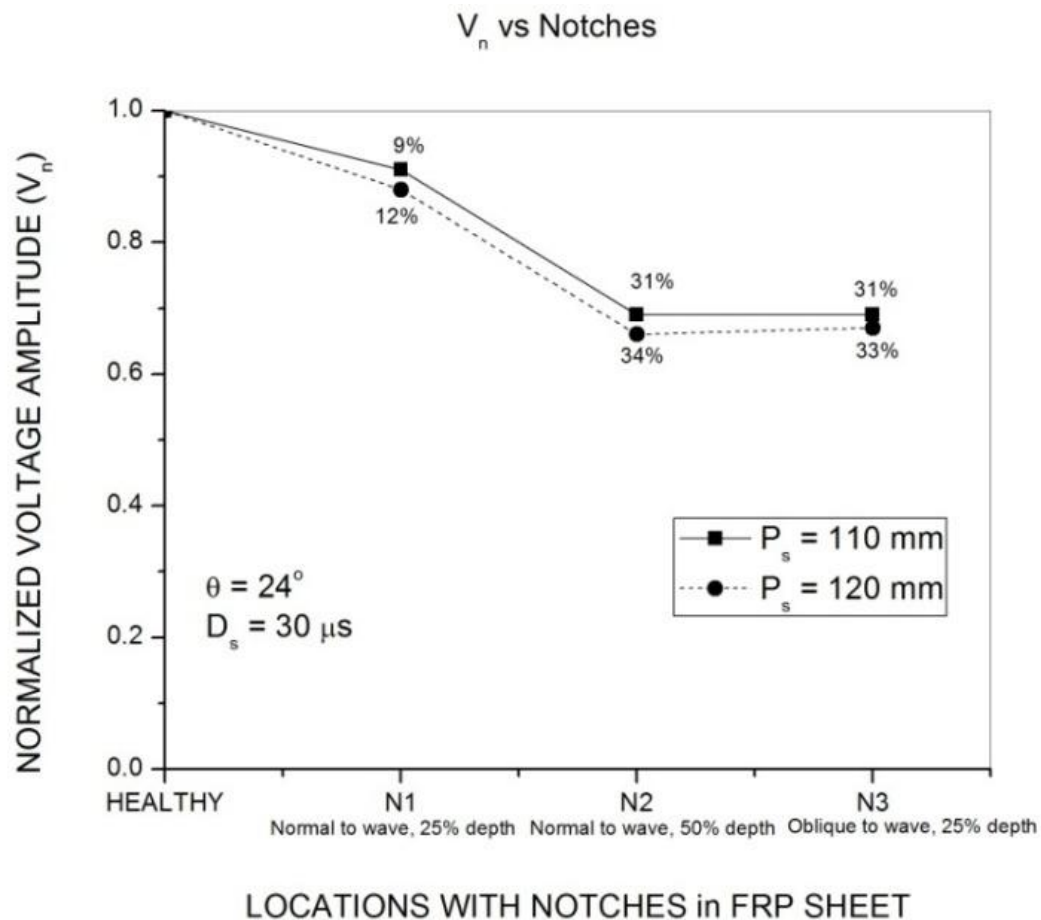


Figure 6.16: Trends of normalized transmitted pulse voltages with different notch depth and orientation

As discussed earlier, the exposure of composite sheets to the marine environment or hygrothermal aging for longer durations results in material degradation. The degraded material sites act as stress concentration points resulting in quick crack initiation, followed by crack propagation and final rupture of the composite. In the present study, this was investigated by scooping out the surface material at various locations and in different orientations with respect to the wave propagation in the GFRP sheet and its effect on the received ultrasonic signals was also investigated. For the healthy regions identified in the submerged EP GFRP sheet, PT signatures were characterized by good signal fidelity and subsequently compared with surface defect locations as shown in Figure 6.17.

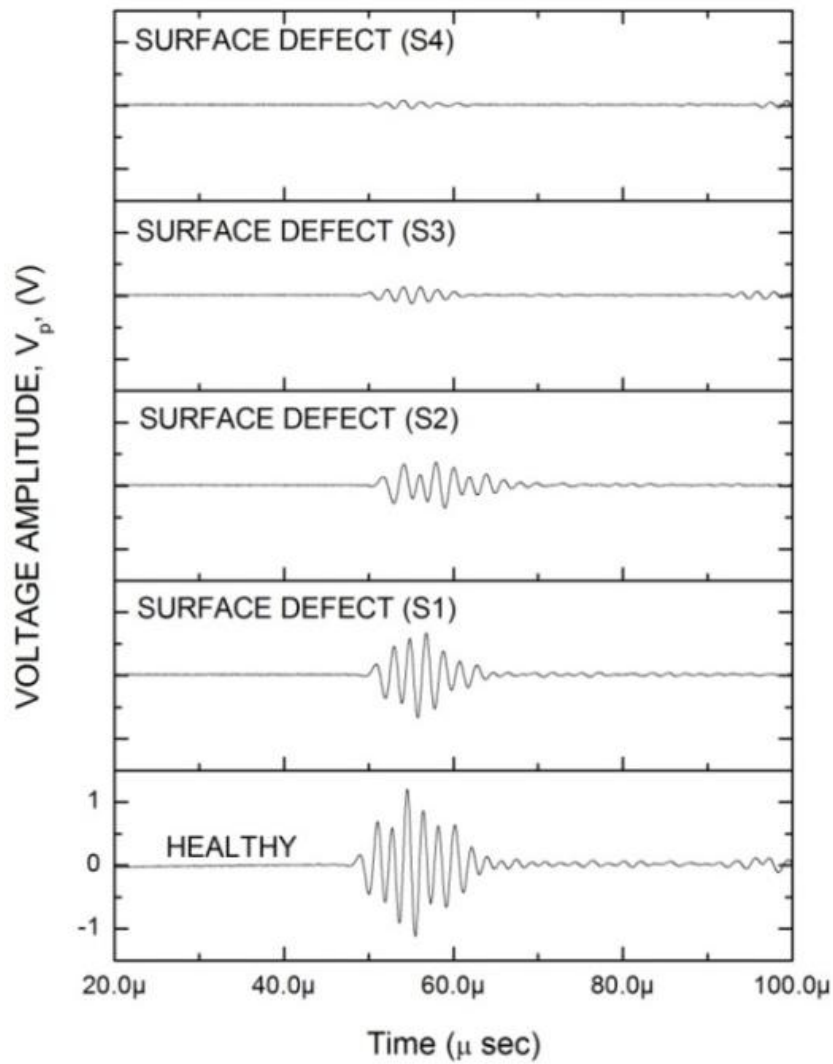


Figure 6.17: Effect on PT signatures with surface defect (S1-S4) vis-à-vis healthy signal

However, in the regions with material loss, a significant drop in voltage of the transmitted signal was observed while the sharpness of the UT signal remained unaltered. At location S1, a drop of 42% in V_n is observed while, at S2 a drop of 69% in V_n is seen compared to the corresponding V_n recorded at a healthy region (Figure 6.18). The significant fall at S2 is likely due to two reasons: direction of surface defect (normal) with respect to the propagating wave and excess removal of material from the surface of GFRP sheet as compared to S1. However, when the surface defect is machined at an angle, the fall in V_n is relatively higher as indicated by the uniform slope of the corresponding trend in Figure 6.18. This fall is observed to be steepest at S4 (94%) due to the excess removal of material from the specimen, visualized as a deeper cut (by naked eye) near that region.

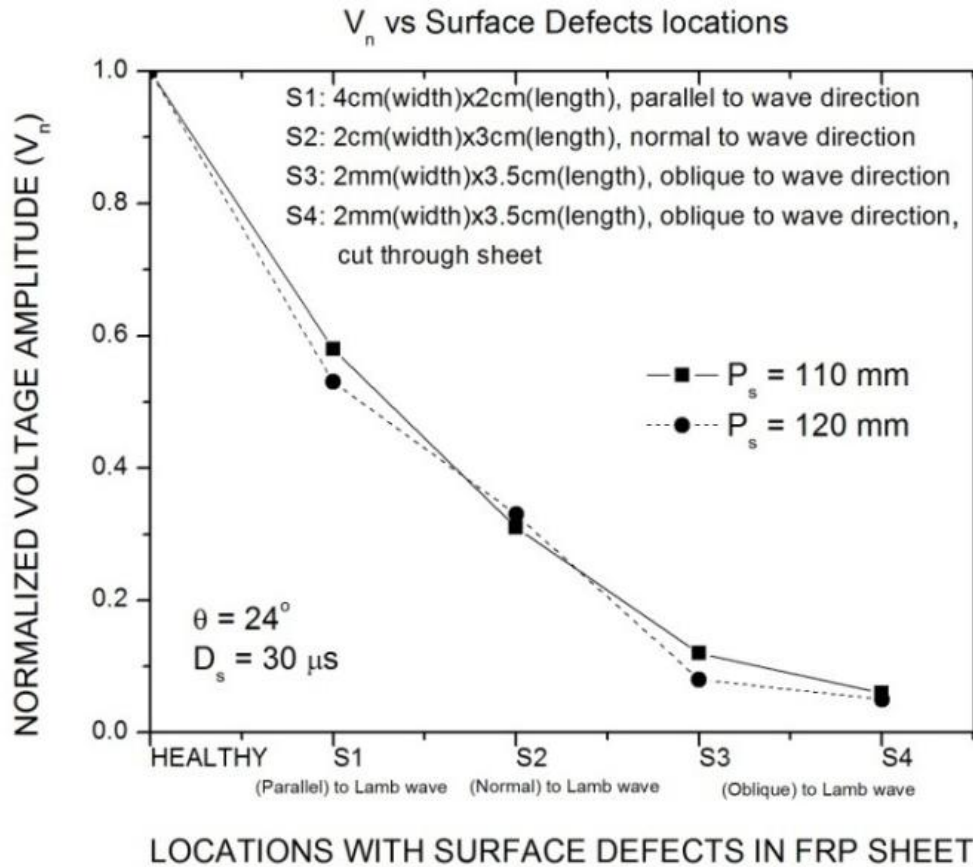


Figure 6.18: Trends of normalized transmitted pulse voltages with different surface defects

It is therefore, possible that the guided wave propagated through the sheet, but only a small portion of the transmitted wave was received by the receiver probe. On further increasing the P_s to 120 mm, the behavior of V_n follows a similar trend as observed for $P_s = 110$ mm. Therefore, the non-uniform loss of material from the surface results in signal attenuation due to the scattering of waves. It is well depicted by a fall in the voltage amplitudes of the received pulse with increasing loss in material degradation. PT scanning of the composite sheet in submerged state with varying material degradation due to usage indicates that any material degradation in the GFRP sheet is well picked up by fall in transmitted signal strength and can be easily picked up. The guided wave methodology has the potential and the ability to pick up degradation due to usage of imperfections in the prepared EP GFRP sheets marked by a fall in signal strength.

Carefully generated specific Lamb wave modes can be used to characterize the presence of manufacturing defects and in-service damages and quantify the severity of defects in submerged GFRP composites by implementing the proposed *in-situ*, non-contact and non-invasive ultrasonic technique.

6.7 Methodology validated in CNT GFRP laminate

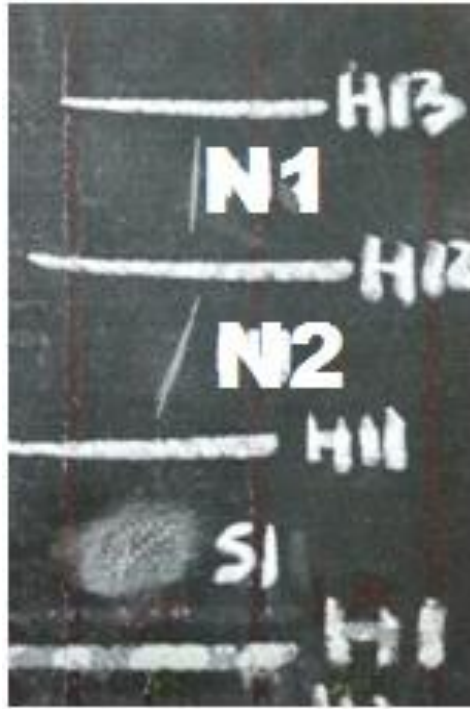
The methodology developed above was also tested on CNT GFRP laminates (refer to Figure 6.19) and interestingly, similar behavior was seen in signal fidelity with respect to usage defects in the sheet. However, there was significantly higher signal attenuation in healthy regions likely due to the matrix modification with nano-fillers as compared to EP GFRP sheet.

In the prepared CNT GFRP laminate as shown in Figure 6.19a, the effect of increasing notch depth and orientation of the notch on ultrasonic signal strength has been investigated with respect to healthy signal. N1 refers to a vertical notch machined having 0.5 mm width and a depth of approximately 20% of sheet thickness while N2, consists of a notch with same width but, with an increased depth of 30% of sheet thickness inclined at an angle of 75° to the horizontal. PT signatures were recorded for healthy (before notch machining) and after the machining of notches N1 and N2 in the laminate.

Figure 6.20a shows the effect of machined notches of varying depths and orientation on the received UT signal amplitude vis-à-vis their respective healthy signals. It clearly illustrates

that as the combined effect of orientation and depth of notch increases, voltage amplitude of UT signal decreases. Similar behavior was also seen for notches introduced in EP GFRP sheet (as discussed in Section 6.5.2.1).

(a)



(b)

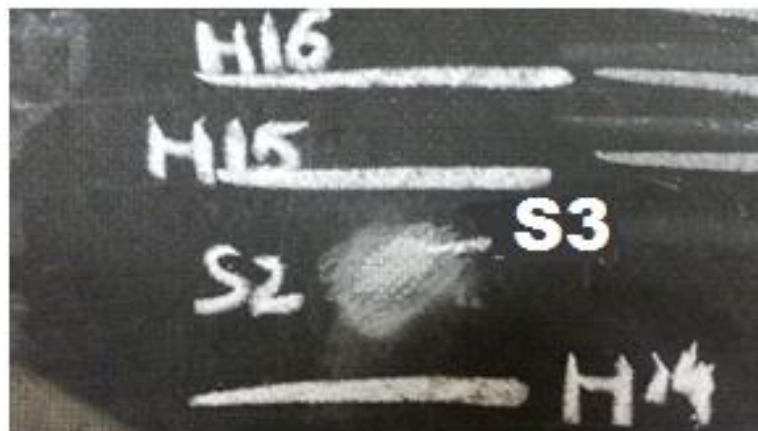
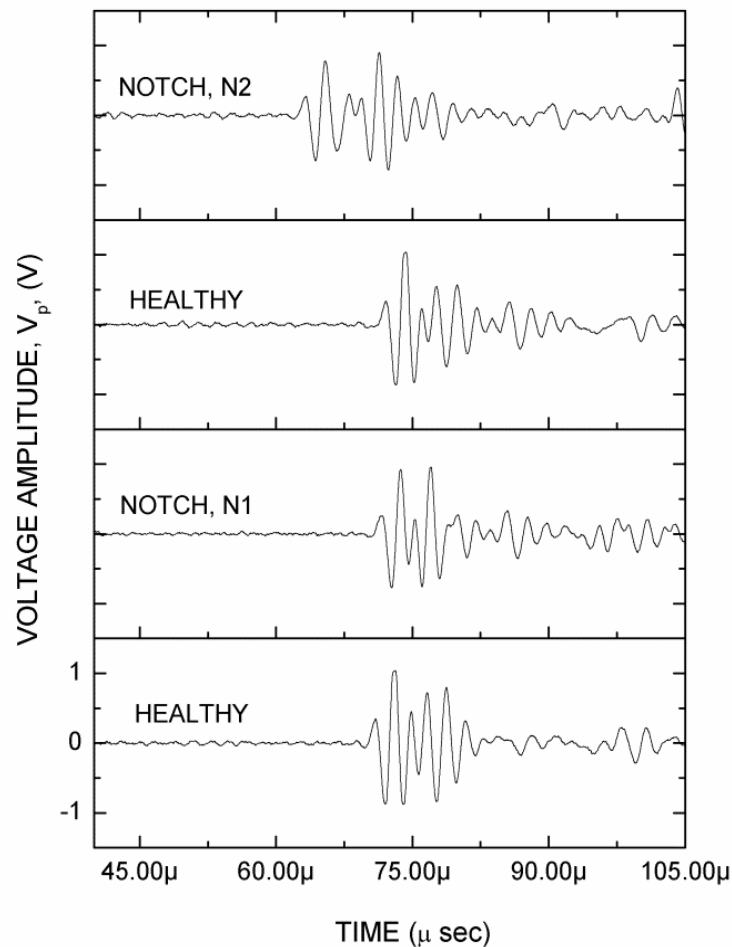


Figure 6.19: (a, b) Actual photograph of CNT GFRP laminate depicting usage defects (notches and surface abrasion)

It is possibly due to the increased reflection and scattering of the Lamb waves from the vertical wall of the notch. The fall in voltage amplitude for an inclined notch (N2) with 10% more notch depth as compared to N1, shows 11% drop in V_n with respect to its healthy signal and thus, establishes the repeatability of the experimental set-up. Hence, this methodology provides with a non-contact, non-invasive technique to identify internal cracks in thin laminates.

As discussed earlier, the exposure of composite sheets to aquatic surroundings for a long time results in material degradation. In this study, surface abrasion was simulated by scooping out the material from the surface at locations S1, S2 and S3.

(a)



(b)

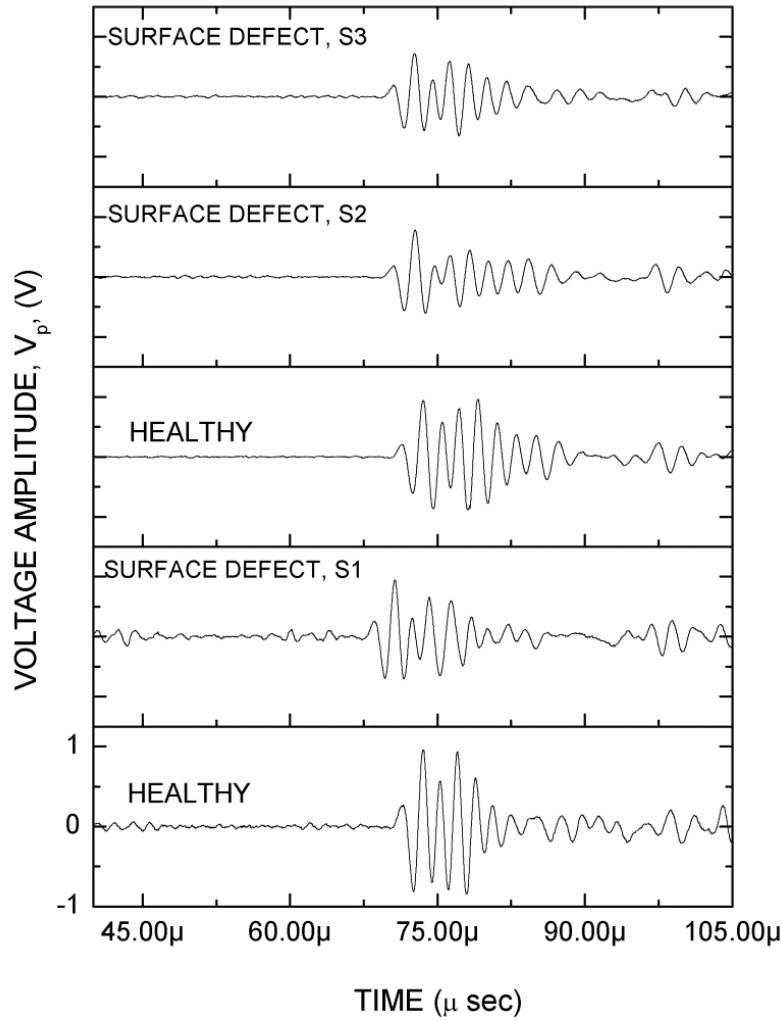


Figure 6.20: Effect on PT signatures: (a) with notches (N1- N2), (b) surface defects (S1-S3) vis-à-vis healthy signal

The location S1 (refer to Figure 6.19a), S2 and S3 (refer to Figure 6.19b) depict regions which are inclined to the propagating wave (with dimensions: width = 1.5 cm and length = 1 cm) and having depths of 15%, 55% and 60%, respectively. The effect of material removal on the received ultrasonic signals has been investigated. In the submerged CNT GFRP laminate, healthy regions were identified as H1 (for S1) and H14 (for S2 and S3) and recorded PT signatures illustrated good signal fidelity. Subsequently the healthy signatures were compared with surface defect locations (S1 – S3) as shown in Figure 6.20b. It is quite evident that in the regions with

material loss, a significant drop in voltage amplitude of the transmitted signal was observed while the sharpness of the UT signal remained unaltered.

At location S1, a drop of 8.5% in V_n was observed while, at S2 a drop of 24% in V_n was seen as compared to the corresponding V_n recorded at healthy region as seen in Figure 6.21.

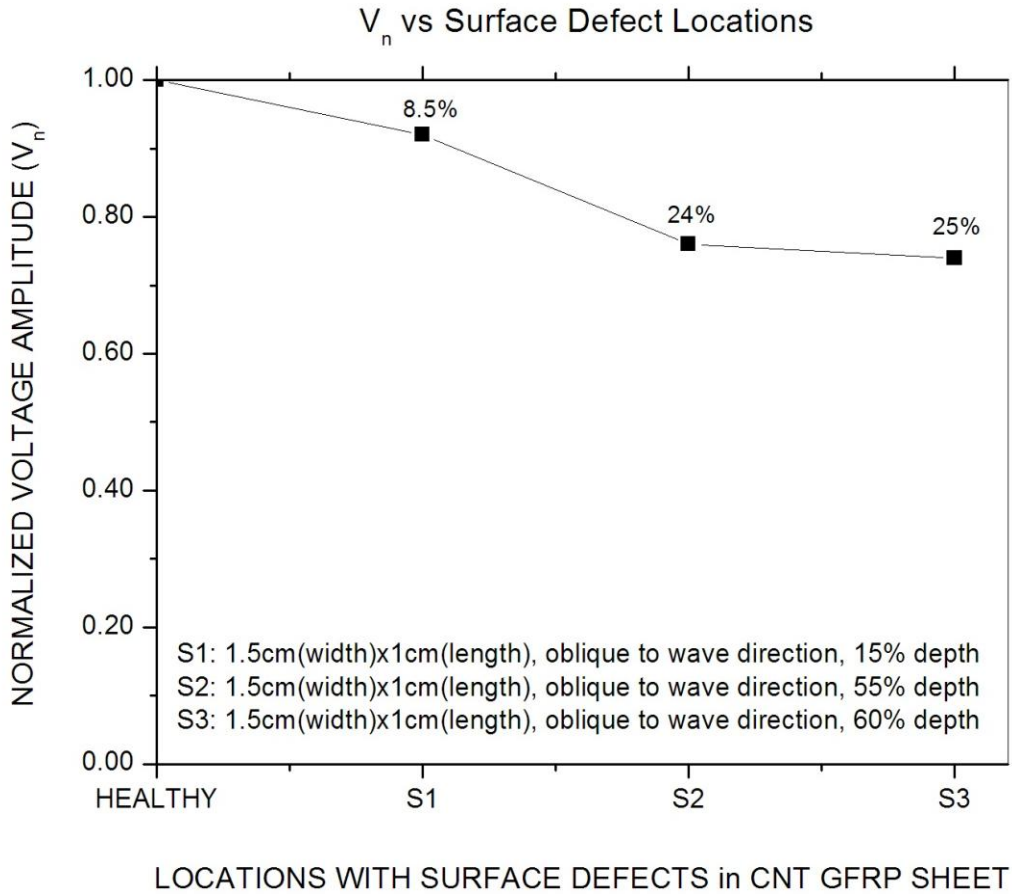


Figure 6.21: Trends of normalized transmitted pulse voltages with different surface defects

The drop in V_n at S2 is likely due to the excess removal of material from the surface of the CNT GFRP sheet as compared to S1. Interestingly, more surface abrasion as seen at location S3 (refer to Figure 6.19b), causes a further drop in signal strength as compared to S2. These results are similar to those found in EP GFRP sheets. Therefore, it can be stated that any material degradation in the GFRP sheets are well picked up and severity is reflected by a fall in transmitted signal strength. The guided wave methodology has the potential and ability to pick

up material degradation which could be either due to usage or imperfections in the prepared GFRP sheets, marked by fall in signal strength.

6.8 NDT of hygrothermal specimen

In Chapter 5, it was seen that different types of damages and material degradations occur in EP GFRP composite during the in-service operation of the composite components in marine structures. The presence of manufacturing defects and in-service damages has been successfully monitored by using Lamb waves as discussed previously.

But, to extend the scope of the research study further, specific ultrasonic guided waves were used for structural health monitoring of hygrothermally conditioned specimens. EP GFRP specimens were immersed in SW at 40°C for 7, 15, 30 and 60 days aging durations. Further, a relation between the changes in properties with the respective ultrasonic signal strengths for varying immersion times has been explored in this study.

Studies have reported a correlation between weight change, mechanical behavior and immersion time [Ray 2005, Gellert and Turkey 1999, Kar *et al.*, 2008, Surathi and Karbhari 2006, Krawczak and Pabiot 1995, Davies *et al.* 2001, Aktas *et al.* 2002 (a, b), Mula *et al.* 2006, Aldajah *et al.* 2009, Prolongo *et al.* 2012, Zafar *et al.* 2012, Chakraverty 2013, 2015].

Therefore, this study provides an insight in the performance and durability of composite laminates under hygrothermal conditions and the results from this study could be used to investigate the performance of real time GFRP components subjected to similar environmental degradation.

6.8.1 Results and discussion

6.8.1.1 Destructive tests

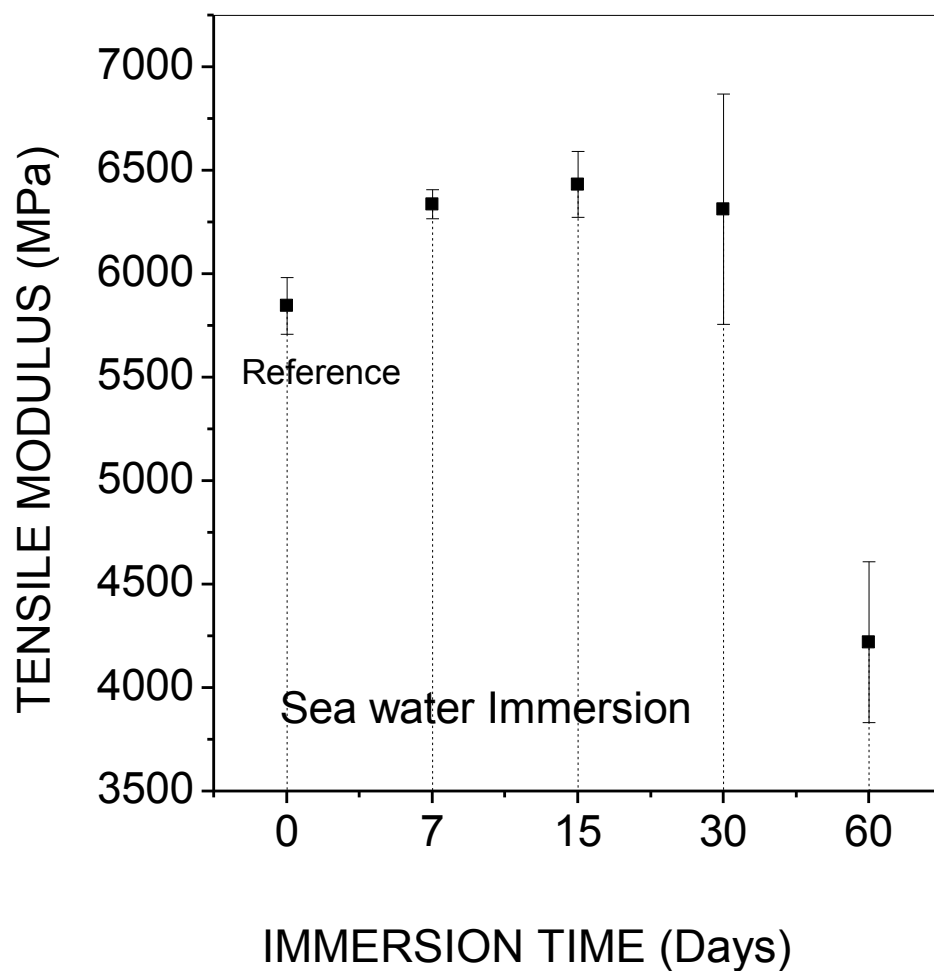
The objective of this section is to investigate the effects of hygrothermal aging on tensile properties of the EP GFRP composites. The average mechanical properties of the conditioned and unconditioned samples obtained by the destructive tensile tests are shown in Figures 6.22(a and b).

Figure 6.22a depicts an increase in tensile modulus of the EP GFRP composites up to 15 day immersion and a maximum decrease after 60 days of aging in seawater. Whereas, tensile

strength and strain at break shows a deteriorating trend over the aging duration as demonstrated in Figure 6.22b. The consistent drop in strength reflects the weakening of the fibre - matrix interface.

It is evident from the figure that the tensile strength and strain values dropped by approximately 30% as compared to the reference (unaged) specimens after 7 days aging time. A similar drop was also seen for strain at break for the same aging time. The drop in strain of the conditioned specimen suggests the plasticization effect of matrix causing material degradation (possibly breaking of bonds in the cured epoxy network) induced by the absorption of non-homogenous flow of water into the epoxy matrix, as also reported by other researchers [Zafar *et al.* 2012].

(a)



(b)

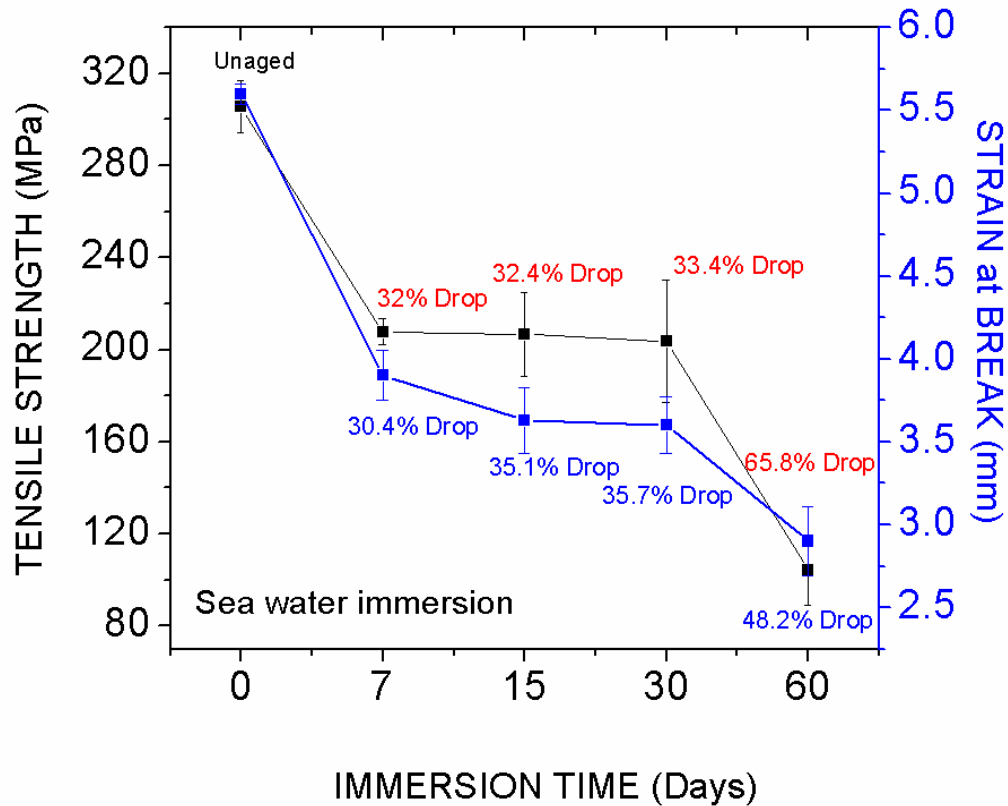


Figure 6.22: Tensile properties of EP GFRP specimens both unaged (reference) and immersed in SW for over 60 days: (a) modulus, (b) strength and strain at break

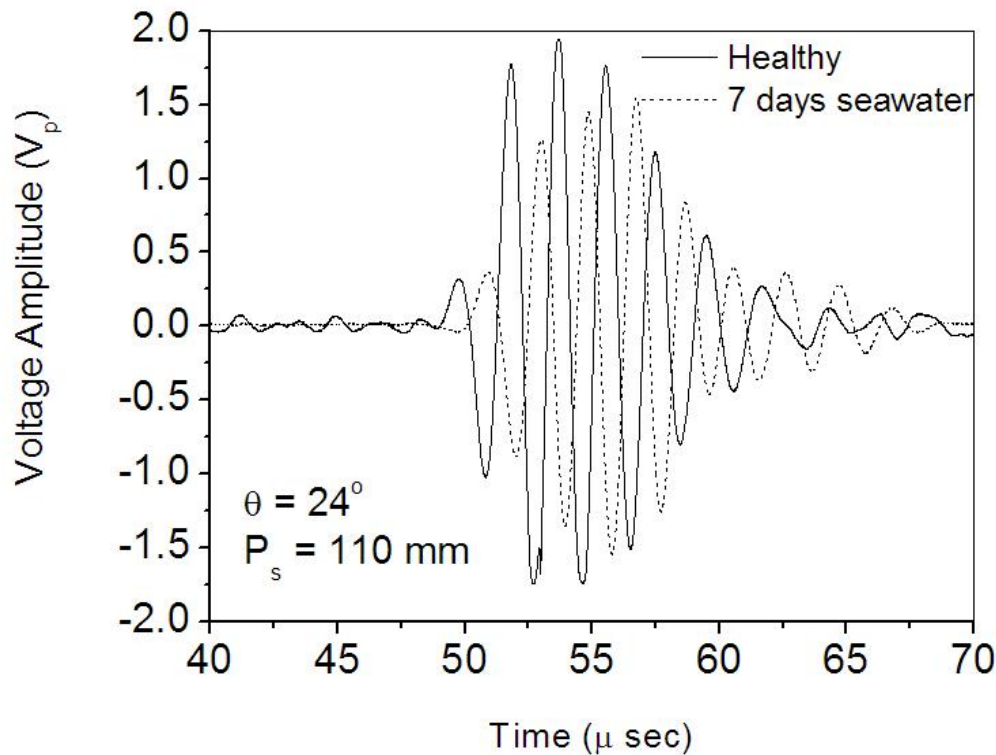
Additionally, the significant decrease in properties indicates that there was a fast absorption mechanism between the surrounding SW and surface of EP GFRP composite. However, the fall in mechanical properties after 30 days of immersion, lies within the error bars of experimental data recorded after 15 days of SW immersion, thus indicating no significant change and stabilization of properties as the samples approach towards equilibrium moisture content. After this plateau region, the EP GFRP specimens immersed for a prolonged aging duration, i.e. 60 days shows a substantial drop in the mechanical properties, i.e. 48% reduction in strain and 66% in the tensile strength (Figure 6.22b). The reduction in ultimate tensile strength shows the effect of plasticization, which tends to soften the polymer when it is exposed to SW for longer span. Therefore, it is assumed that the poor interfacial bonding between the matrix and the glass fibres, is the predominant factor causing the degradation of the tensile properties of EP GFRP specimens when immersed in SW conditions for longer periods of time.

6.8.1.2 Guided wave investigations

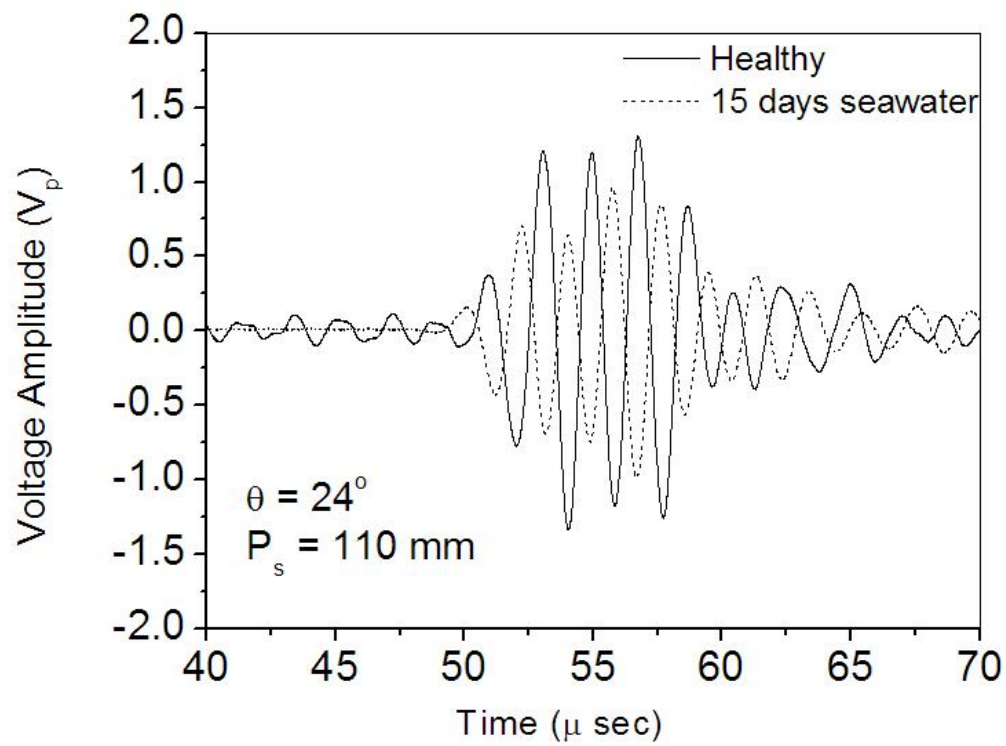
In the last section, the effect of hygrothermal aging on composites has been observed with respect to their mechanical properties. Further, an attempt has been made to relate the effect of weakening fibre-matrix interface on the voltage amplitude of leaky Lamb waves propagating through the specimen. Specific leaky Lamb wave mode with good signal strength were recorded in healthy EP GFRP laminate specimens by choosing the appropriate experimental parameters such as θ , D_s and P_s (as described in Section 6.4) along with other pulser receiver settings. The ultrasonic transmission signatures in Figure 6.23 show the effect on signal strength with respect to their respective healthy signals (prior to the immersion of samples in SW) over the increasing aging period. Since each composite specimen was unique, hence, a healthy signature was taken for each specimen prior to SW immersion for different periods.

The ultrasonic signatures recorded in pitch-catch mode for specimens subjected to SW for 7, 15, 30 and 60 days (Figures 6.23 a-d) shows a reduction in signal amplitude, V_p , as compared to their respective healthy signals.

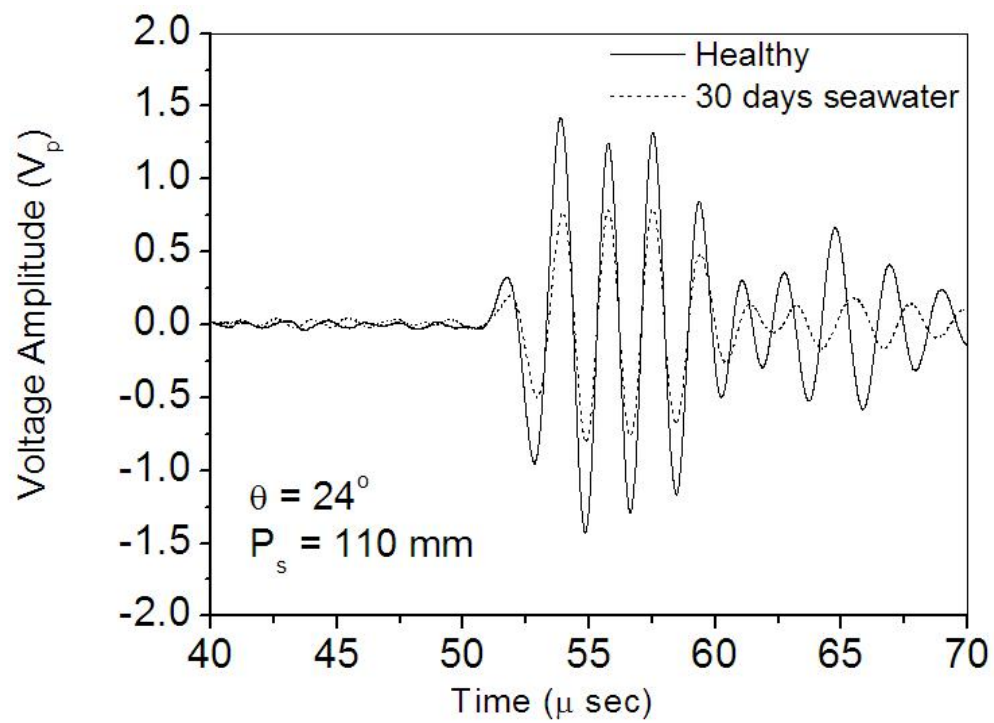
(a)



(b)



(c)



(d)

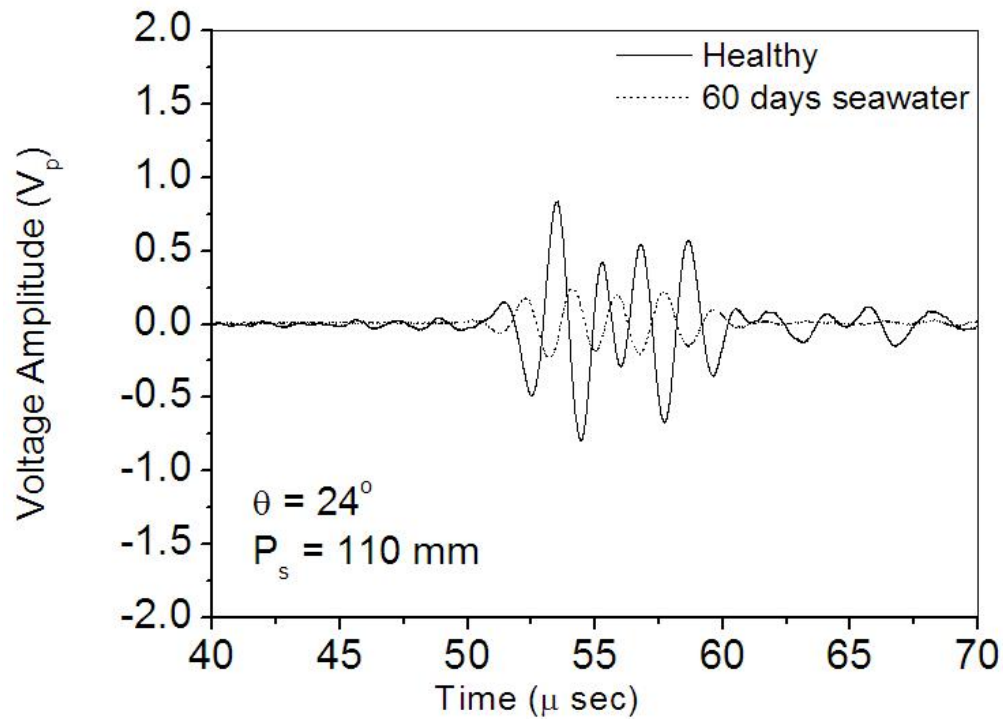


Figure 6.23: Ultrasonic signatures in specimens exposed to SW after: (a) 7 days, (b) 15 days, (c) 30 days, (d) 60 days of immersion

From the signatures obtained at varying ages of hygrothermal loads, it is observed that the signal attenuates rapidly with increasing exposure time. During the first 7 days of exposure, the signal dropped comparatively less as compared to samples aged for 30 and 60 days where, the drop observed is consistently higher. This indicates to an increase in internal imperfections because of degradation in the specimens due to water infusion. The matrix degradation could possibly be due to plasticization of the resin in the initial stages followed by swelling of the matrix which further deteriorated the fibre-matrix interface.

Figure 6.24 represents the percentage drop in signal strength for three different specimens conditioned for varying periods of immersion of 7, 15, 30 and 60 days. The results in Figure 6.24 noticeably indicate an increasing trend of the percentage drop in signal strength as the duration of specimens in the SW increased. The trend is found to be similar for all three different conditioned specimens with varying immersion periods, thus illustrating reproducibility of the ultrasonic set-up.

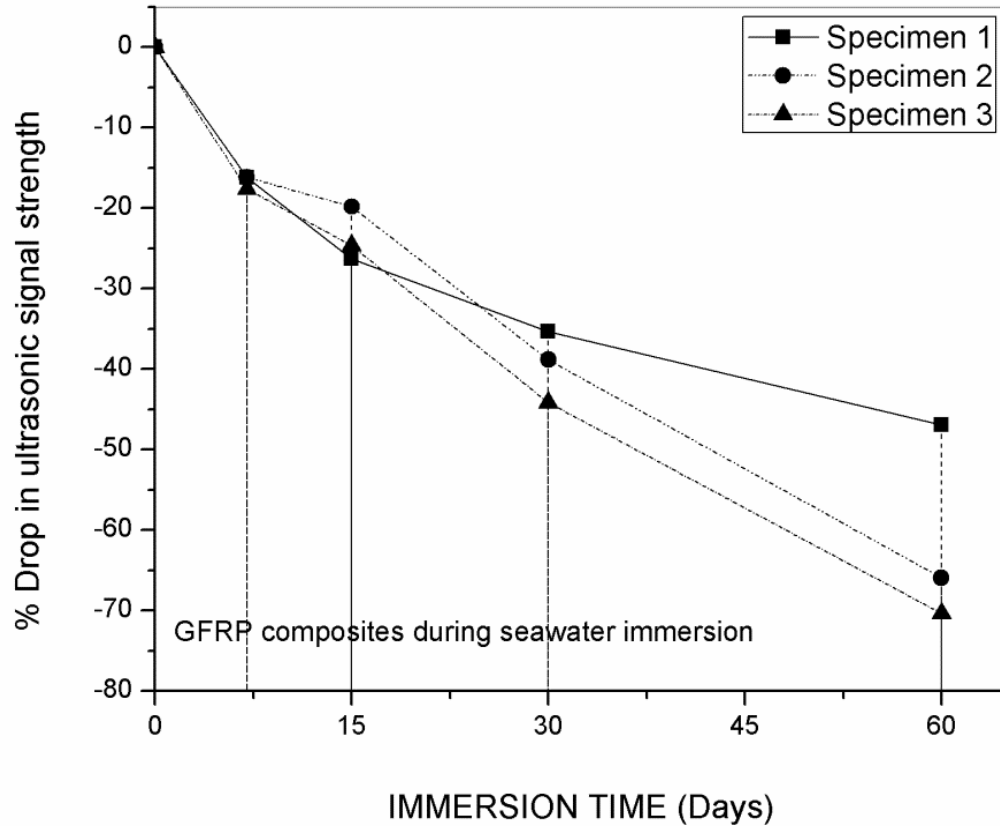


Figure 6.24: Percentage drop in ultrasonic signal strength of EP GFRP composites on increasing seawater immersion time

Furthermore, a comparison of the effect of hygrothermal aging on the ultrasonic signal drop and percentage weight gain is attempted in Figure 6.25. The weight gain by EP GFRP composite increases by more than 60% in the first 15 days likely due to capillary action, but as the water inside the matrix tends to reach an equilibrium state the weight gain dips slightly (after 30 days of immersion). However, the diffusion of water into the fibre-matrix interface results in further sorption of water molecules and thus resulting in weight gain as shown in Figure 6.25. On the contrary, the percentage drop in ultrasonic signal strength is inversely proportional to the weight gain and immersion time, i.e. signal strength drops when more amount of water got infused into the composite interface which itself is a function of time. Therefore, it may be concluded that non-destructive ultrasonic tests can provide an adequate means for evaluating the effects of hygrothermal environment on prolong exposure of the EP GFRP composites.

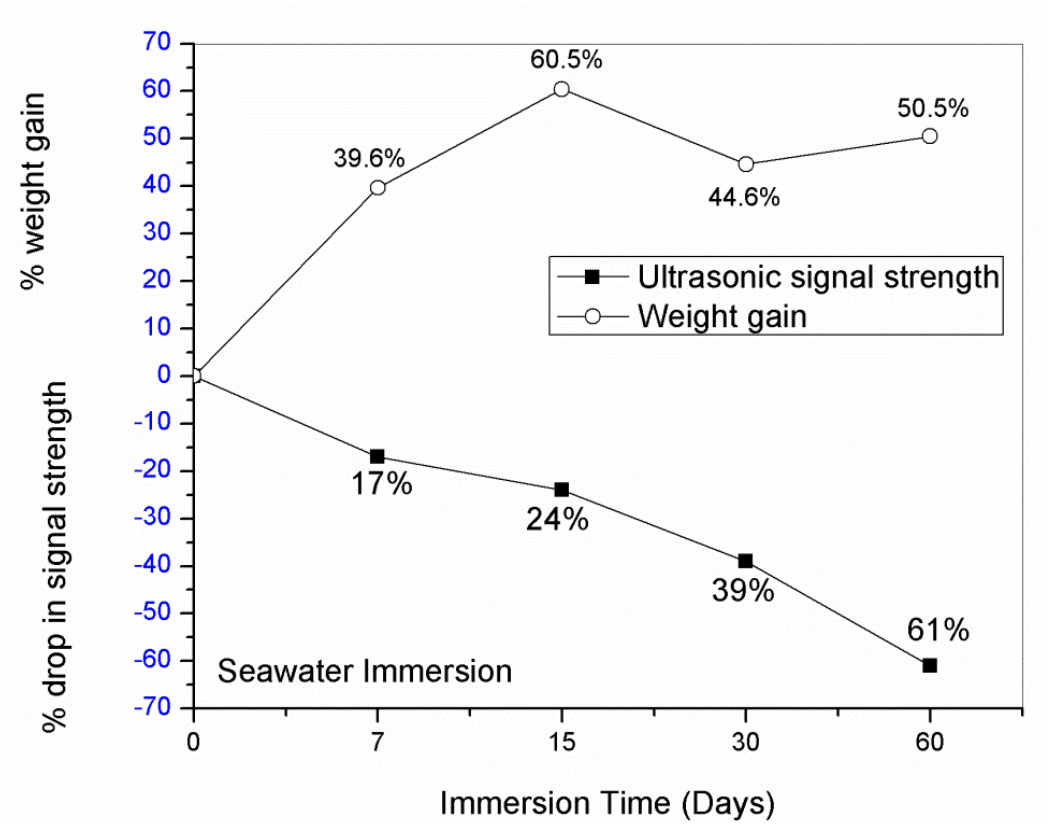


Figure 6.25: Comparison of ultrasonic signal strength with % weight gain in EP GFRP specimens up to 60 days of immersion

Also, the effect of drop of signal in terms of signal amplitudes (V_p) has been correlated with the drop in tensile strength and strain at break when subjected to a hygrothermal environment for different periods (Figure 6.26).

During the initial 7 days of immersion, the tensile strength reduced by 32%, which further dropped to 66% after 60 days. A similar trend was also visible for strain to break, which reduces to 50% after 60 days of immersion time. The percentage drop in transmission signal strength is also observed to be 17% after 7 days that increased to 61% after 60 days of exposure in SW, as seen for tensile strength. It is interesting that the loss in amplitude correlates with the decreasing tensile strength & strain to break quantitatively. The possible reasons for decrease in tensile properties have been discussed previously in this chapter. Also, the decrease in peak to peak voltage amplitude is likely due to loss of adhesion or de-bonding at the fibre-matrix

interface, moisture absorption, matrix swelling and chemical attack on a matrix and fibre which results in greater attenuation of the signal.

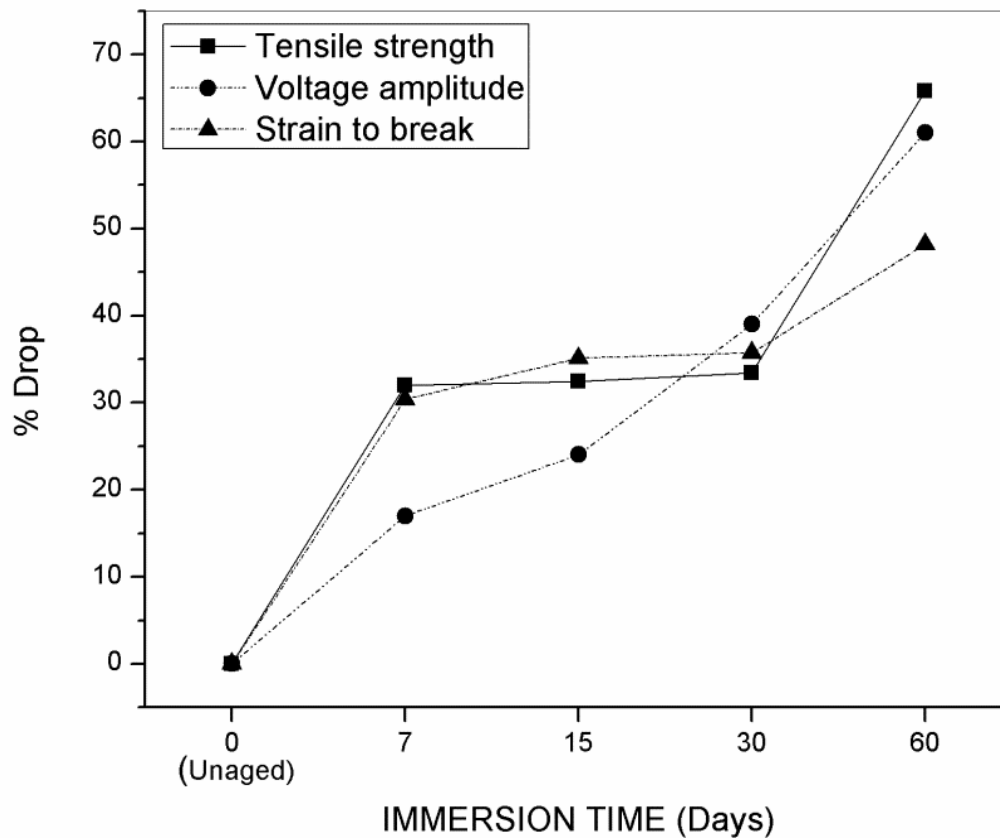


Figure 6.26: Comparison of tensile strength, strain and V_p with increasing SW immersion

Hence, the drop in ultrasonic signal strength can be used to relate the loss in mechanical properties of the EP GFRP laminates with non-destructive voltage amplitude under hygrothermal loading. Non-destructive ultrasonic measurements in the future will serve as an indicator of corresponding loss in tensile strength with aging and will facilitate non-destructive evaluation of GFRP laminates under SW immersion.

6.9 Closing remarks

By using a pair of mobile immersion probes wherein, specific Lamb wave modes were generated and both manufacturing and usage defects in EP GFRP laminates were monitored under submerged conditions. The transmitted signal strength dropped when the Lamb wave interacted with these defects, but the sharpness and time of flight of the received signal remained

unaffected by the presence of these defects in GFRPs. A similar behavior of loss in ultrasonic signal strength on encountering defects in CNT GFRP laminates was also witnessed. Lastly, an attempt was made to investigate the effect of hygrothermal aging on ultrasonic voltage amplitude signals. The experimental results revealed that the ultrasonic voltage amplitude drop correlates well with a fall in tensile strength as immersion time increases. Therefore, this method can be exploited as an effective damage monitoring technique which also has the potential to develop into an *in-situ* and non-invasive health monitoring tool. Thus, this technique can serve as an effective method to diagnose the service life of marine vessels while they are in operational mode.

Chapter 7. Optimal curing conditions of CNT modified GFRP composites

7.1 Introduction

In chapter 3, curing mechanism between epoxy resin and hardener was discussed where; several parameters affecting the cured material were reported. But in recent years, CNTs have gained a considerable interest globally because of its excellent properties (both mechanical as well thermal). Epoxy resin - a thermoset matrix, has been commonly used as polymer matrix to prepare advanced composites as it has the flexibility of tailoring it for a variety of applications. The properties of neat epoxy composites are mostly improved by the incorporation of nano-fillers but sometimes due to their poor dispersion and weak interfacial bonding the mechanical properties are lowered. It is well known that the surface modification of CNTs promotes better dispersion and improves the interfacial bonding with the matrix. The surface modification schemes such as exposure to ozone gas [Najafi *et al.* 2006, Sham and Kim 2006, Li M *et al.*, 2008, Tang *et al.*, 2011] or by introducing active polar groups (for example carboxylic, amino, fluorine etc.) on the side walls have shown uniform dispersion and chemical interaction with an epoxy matrix [Gojny and Schulte 2004a, Titus *et al.*, 2006, Ma *et al.*, 2010, Rahman *et al.*, 2012]. The curing mechanism between the epoxy resin and nanotubes is also believed to be a complex mechanism as it depends on various conditions, for instance: type of epoxy and nanotubes used, dispersion of nanotubes in epoxy, functionality of the curing agent and lastly, the curing conditions [Velasco-Santos *et al.*, 2005, Hosur *et al.*, 2010, Saeb *et al.*, 2013, Cividanis *et al.* 2014, Farbod *et al.*, 2014, Paszkiewicz *et al.*, 2015]. Several studies have been carried out in the past to examine the thermal as well as mechanical behavior of polymer composites reinforced with ACNT [Shen *et al.*, 2007a, Chen *et al.*, 2008, Wang S *et al.*, 2006, Hosur *et al.*, 2010, Gojny and Schulte 2004a, Prolongo *et al.*, 2010, Chandrasekaran *et al.*, 2011, Garg *et al.*, 2015], but the studies related to cure kinetics of epoxy resin with functionalized nanotubes are scarce. Contrary results have been reported for the thermal behavior of nanocomposites, with the main focus being on T_g of epoxy matrix, which is observed to either increase or decrease by incorporating ACNT [Liu and Wagner 2007, Allaoui and Bounia 2009]. An increase in T_g is likely to be associated with the hindrance in mobility of epoxy resin moiety

on interaction with amino groups [Farbod *et al.*, 2014, Prolongo *et al.*, 2010]. Besides this, the increase in T_g may also be associated with the presence of nanotubes in epoxy resin which causes an acceleration effect in the early stages of curing.

Apart from thermal properties, the effect of curing on mechanical properties is equivalently important. In general, the mechanical behavior of epoxy composites is affected by the curing reaction with either amine hardener or nano-fillers [Velasco-Santos *et al.*, 2005, Farbod *et al.*, 2014]. Specifically, the reaction of epoxy resin with amine hardener (as shown earlier in Figure 3.2), reveals that the primary amine hydrogen acts as a nucleophile and opens the epoxide ring which subsequently produces secondary amine. These secondary amines further interact with other epoxy rings and consequently form a long polymer chain, while releasing hydroxyl groups during the reaction. These hydroxyl groups tend to form ether links and this process is referred as etherification. The mechanism for which is illustrated in Figure 7.1. The etherification competes with the epoxy-amine curing reaction, and depends upon the curing temperature and epoxy: amine ratio in the composites reinforced without nano-fillers.

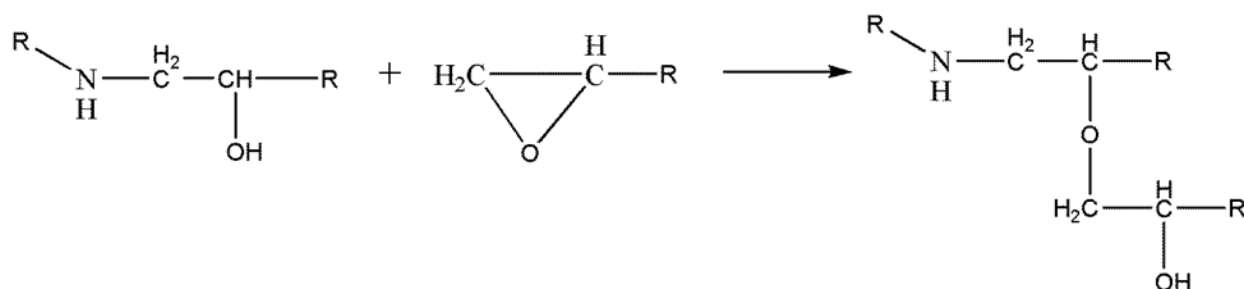


Figure 7.1: Illustrating the mechanism of etherification reaction [Source: Saeb *et al.*, 2013]

As stated earlier, apart from amine hardener, the curing mechanism is also influenced by the addition of carbon nanotubes as nano-fillers. When amino-functionalized nanotubes are mixed in epoxy resin, the amine (polar) groups attached on the sidewalls of nanotubes act as curing agent since, they have a similar chemical structure to amine hardener i.e. the hydroxyl groups catalyzes the ring opening of epoxy resin and thus accelerate the curing process and also result in higher adhesion between epoxy matrix and CNTs. As a result, enhanced interfacial adhesion with the epoxy is attained due to amidation which further affects the T_g of nanocomposites. From the above discussion, it is quite clear that CNT influences the curing process of epoxy resin and a thorough understanding of curing kinetics is vital for the design,

analysis and optimization of manufacturing multi-functional composite laminates. Also, the present trend of the industry is focused on processing, i.e. making the products available at a lower cost. Therefore, it is essential to study this curing mechanism while focusing on finding the relation between T_g of EP GFRP and CNT GFRP composites along with its effect on the thermal and mechanical properties.

Different characterization techniques can be used to monitor the curing kinetics of the composite, but the most widely used technique is DSC. It is because of its practicality and several pieces of information obtained from one sample. The most important use of this technique is when 'n' number of heating cycles of the same sample are performed and a clear change in exothermic/enthalpy peak and T_g of the composite material is observed.

Thus, the objective of this work is (i) to study the influence of amino-CNTs on the cure behavior of epoxy composites, (ii) to determine the optimal curing schedule for ACNT reinforced epoxy composites, (iii) to fabricate and mechanically test the GFRP composites (with different matrix compositions) using the optimal curing schedule. (iv) Lastly, to examine the effect of surface treatment of glass fibre with organosilanes in modified matrix.

7.2 Characterization

DSC measurements were made by scanning the samples between 45°C and 250°C at 10°C/min heating rate. Once the cooling was attained, the specimens were thereafter subjected to heating/cooling cycles to determine the extent of the uncured epoxy nanocomposite left. The TEM analysis was carried out on Hitachi (H-7500) operating at 110 kV. The fully sonicated liquid sample was placed onto a copper grid and observed under the microscope. The mechanical properties had been evaluated by using Universal Testing Machine, Zwick Roell Z010. The tensile tests were carried according to ASTM D3039 at a crosshead speed of 2 mm/min while the flexural tests were performed at a calculated speed of 1.34 mm/min as per ASTM D790. Since the thickness of the specimen was less than 1.6 mm, the span to width ratio was kept at 25.4 mm as per ASTM recommendations. For each prepared composite composition, 4 samples were tested.

7.3 Results and discussion

7.3.1 Effect of CNT on the curing process

The DSC scans for EP GFRP and ACNT GFRP composites prepared at 70°C for 7 h (as per supplier's recommendation) are shown in Figures 7.2 and 7.3. The occurrence of cross-linking curing reaction in epoxy systems is identified by an enthalpy relaxation peak in the DSC heat flow curve. Interestingly, the enthalpy relaxation peak and the glass transition appeared together for the scanned samples. The T_g was calculated from the first derivative curve of the peak in DSC thermogram. Similar method for determining the extent of cross-linking and glass transition temperature has previously been reported [Rahman *et al.*, 2012]. The graph focusing on the region marked by a rectangle and shown in the inset depicts the enthalpy peak and also the T_g , which for EP GFRP is 69°C.

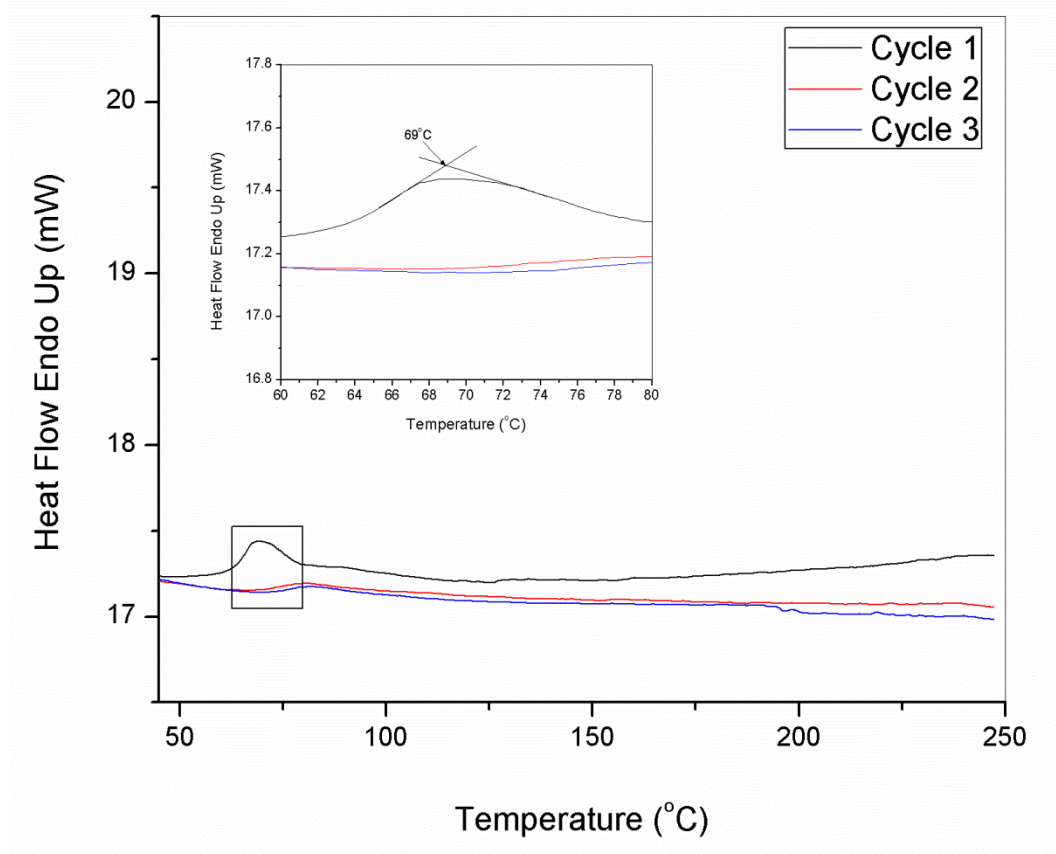


Figure 7.2: DSC thermograms for EP GFRP sample at heating rate of 10°C/min (First, second and third cycle)

The first run means that the DSC is performed for GFRP sample from 45°C to 250°C, whereas second and third run indicates that the DSC is carried out again for the first run sample with the same temperature programs. It can be observed that during the second and third cycle, peak has disappeared, which signifies the complete curing of epoxy after first run. Figure 7.3 shows the DSC thermogram for ACNT GFRP composite. During the first run, the peak appeared at 95°C. The difference in the T_g of EP GFRP and ACNT GFRP samples is due to the presence of CNTs. This confirms that the curing reaction of epoxy is affected by the addition of amino-CNTs. Interestingly, second and third cycle run illustrates a further shift to the right for the enthalpy peak, at approximately 103°C.

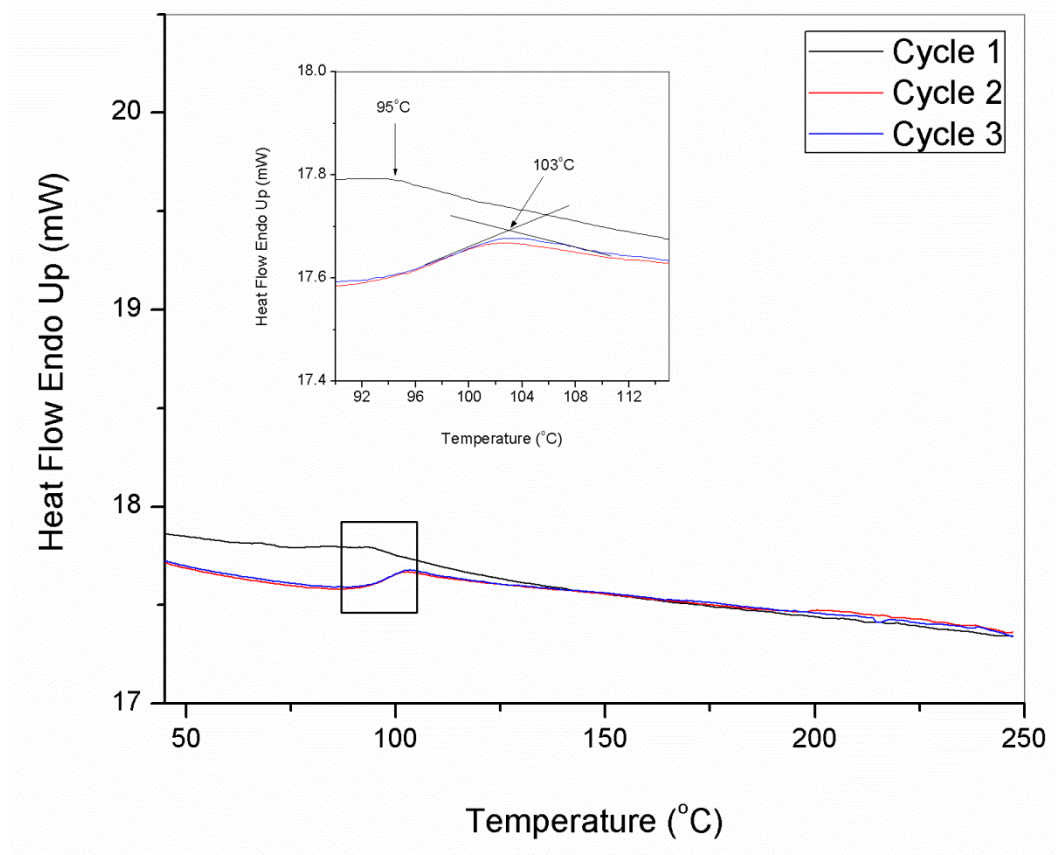


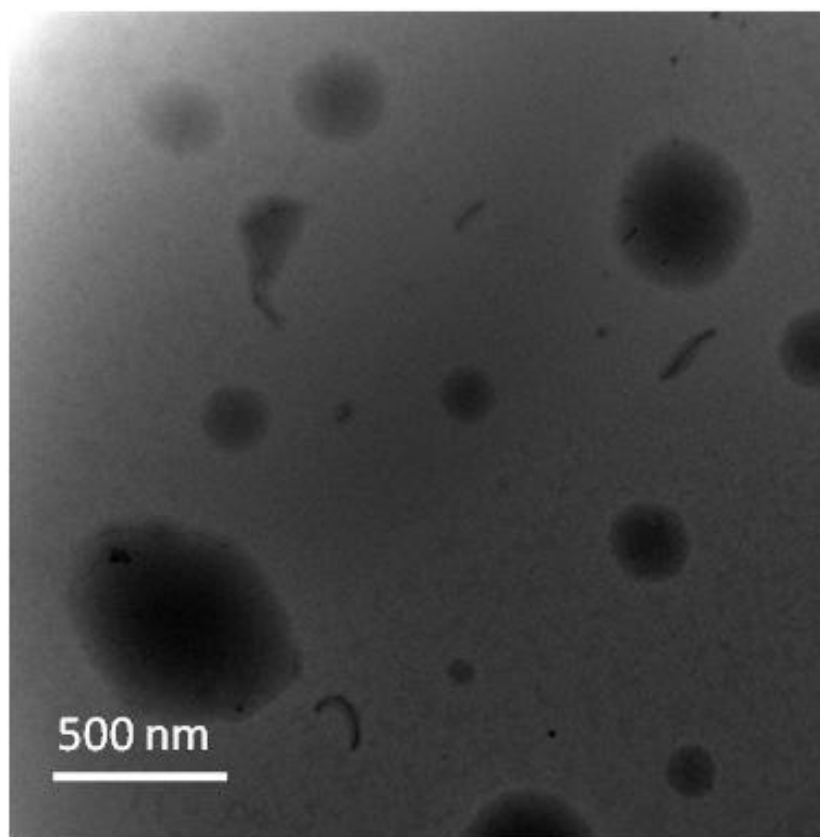
Figure 7.3: DSC thermogram for ACNT GFRP samples at heating rate 10°C per min (First, second and third cycle)

Clearly, there is a shift in glass transition temperature towards higher value for CNT reinforced composites as compared to the EP GFRP sample. There are several factors which explain this shift of T_g of the ACNT GFRP composites: (i) The strong interfacial adhesion

between the ACNTs and epoxy resin inhibits the polymer chain mobility, which tends to increase T_g . The covalent bonding between ACNT and epoxy is evident from TEM image Figure 7.4 and is supported by the FTIR bands at 3431 cm^{-1} (shows stretching of a primary amine group of ACNT), 1581 and 1247 cm^{-1} (corresponds to the N-H in plane and C-N stretching) as evident in Figure 3.8c (of Chapter 3).

Besides this, in Figure 3.8c the absence of epoxide peak at 915 cm^{-1} also confirms the occurrence of polymerization reactions. (ii) ACNT could be considered as polyamine system as it has numerous amino groups on its side-walls and probably multiple moiety bonds together with the nanotube, where it serves as a curing agent and affects the initial curing rate of the composite; (iii) steric hindrance of benzene rings may lower the flexibility of the epoxy resin which further limits its movement and thus increases the T_g of the composite [Shen *et al.*, 2007a, Luo *et al.*, 2012].

(a)



(b)

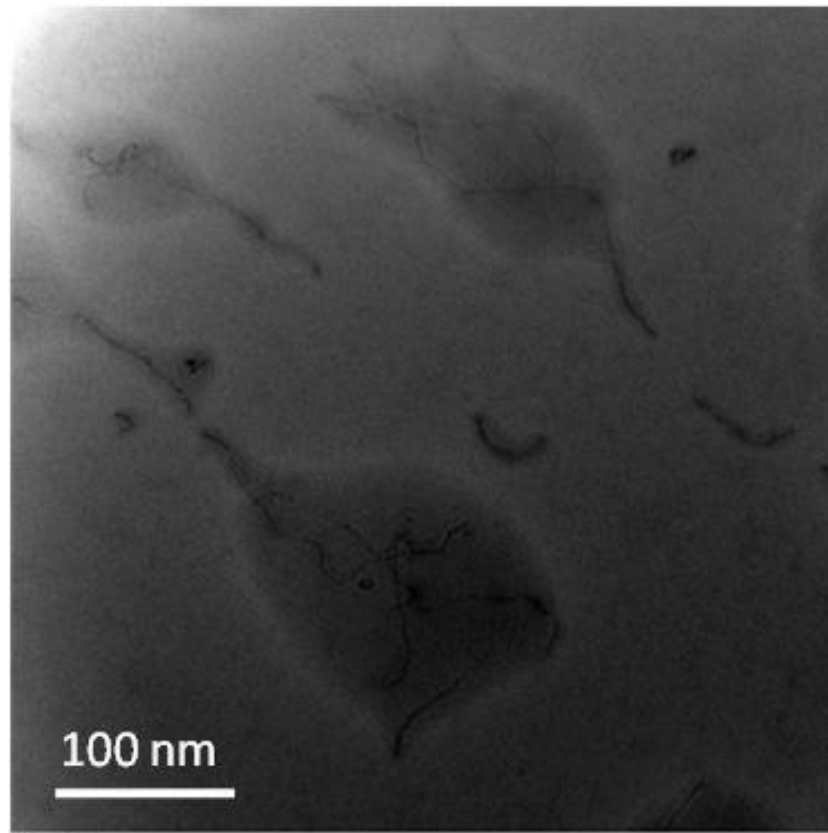


Figure 7.4: TEM image: (a) depicting uniform dispersion, (b) strong interfacial bonding of amino-CNTs with epoxy resin

On the contrary, few studies have even reported a drop in T_g after the addition of pristine or amino-functionalized nanotubes in epoxy resin [Bae *et al.*, 2002, Valentini *et al.*, 2004, Wang Z *et al.*, 2004, Jang *et al.*, 2005, Lijie and JinBo 2006, Shen *et al.*, 2007b, Yang K. *et al.*, 2008, Prolongo *et al.*, 2010] but, due to its complexity, no clear explanation describing this effect has been reported so far.

Consequently, the data obtained from these curves suggest that the epoxy resin curing conditions being followed need to be further explored to obtain a fully cured sample in the first run, i.e. with a negligible change in enthalpy relaxation peak for second and third cycles. Since, this study focuses primarily on the reinforcement of EP GFRP composites with carbon nanotubes, ACNT GFRP composition has been considered for further in-depth investigation of curing conditions. For studying the role of curing conditions on the epoxy-amine curing

behavior, time as well as temperature was varied. The samples were prepared by following the curing schedules listed below after considering a shift in T_g as previously observed in Figure 7.3:

1. 10 h at temperature of 70°C
2. 7 h at temperature of 85°C
3. 10 h at temperature of 85°C

The new sets of samples manufactured using three different curing schedules were evaluated for their respective thermo-mechanical behavior. The findings from this analysis helped to choose an optimal curing schedule to be followed for further experimentation. Figures 7.5, 7.6 and 7.7 show the DSC thermograms obtained after following the above stated curing schedules.

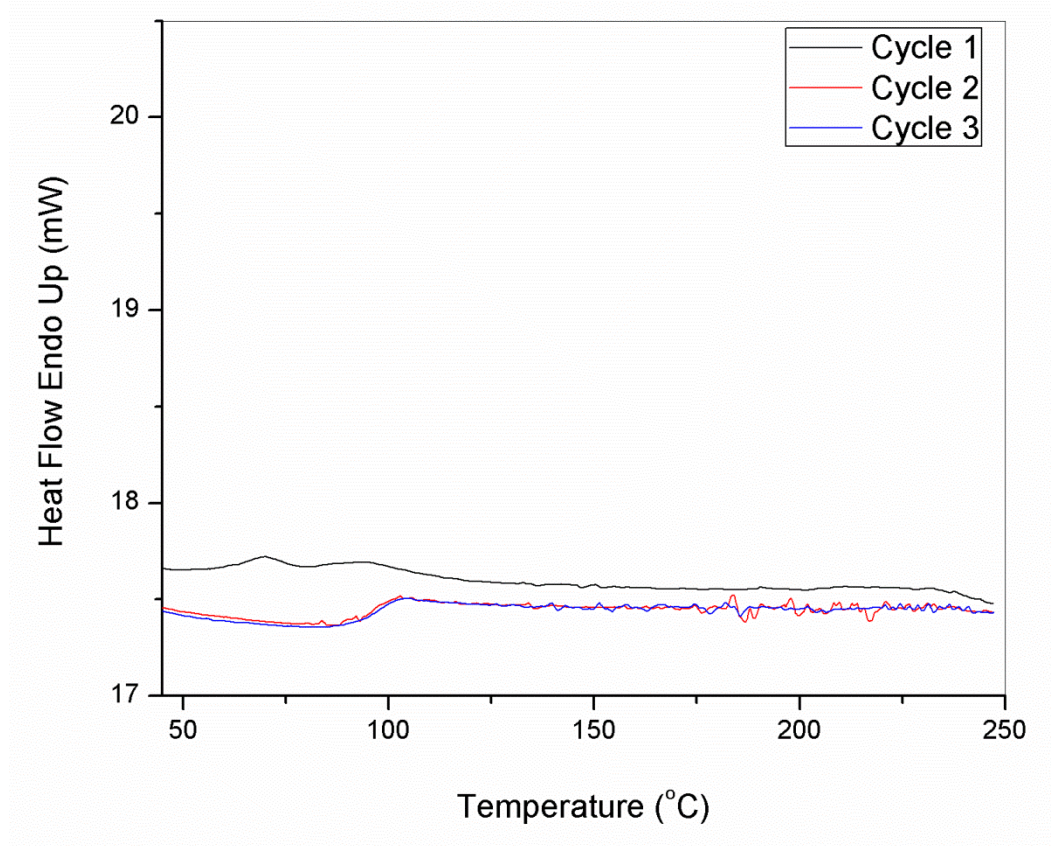


Figure 7.5: DSC thermograms for ACNT GFRP specimen cured for 10 h at 70°C

Among the DSC thermograms obtained for different curing schedules, the curves reveal that epoxy-amine curing was considerably improved as evident by minimal enthalpy relaxation peaks in Figures 7.5, 7.6 and 7.7. Interestingly, complete curing during first cycle run was observed for samples cured at 85°C for 7 h as well as 10 h. However, on comparing DSC thermograms in Figures 7.6 and 7.7 it can be clearly seen that curing schedule of 7h at 85°C shows almost complete curing of epoxy resin during the first, second and third cycle runs whereas, a slightly different pattern is observed for samples cured for 10h at 85°C.

Hence, the calorimetric results obtained from thermal analysis in this study are in accordance with some earlier studies [Gojny and Schulte 2004a] owing to the effect on thermal behavior of GFRP composites by modifying the curing schedule. However, prior to choosing an optimal curing schedule, it is critical to assess their effect on the mechanical behavior.

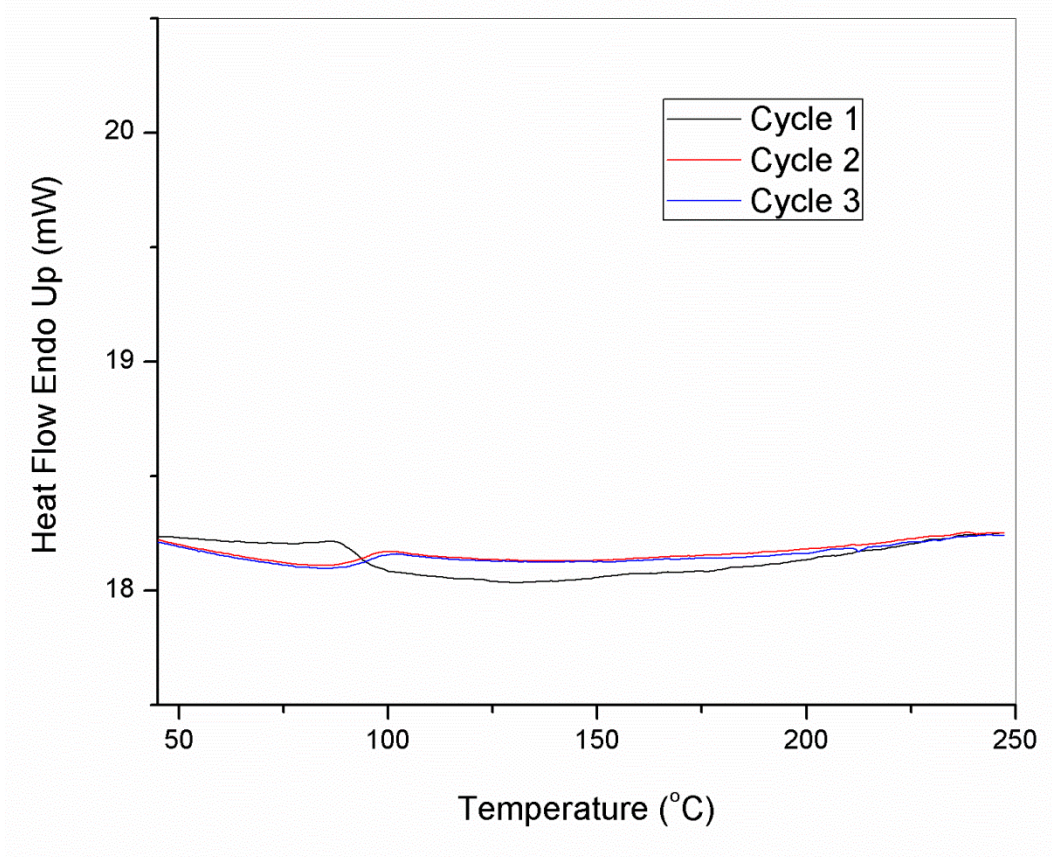


Figure 7.6: DSC thermograms for ACNT GFRP specimen cured for 7 h at 85°C

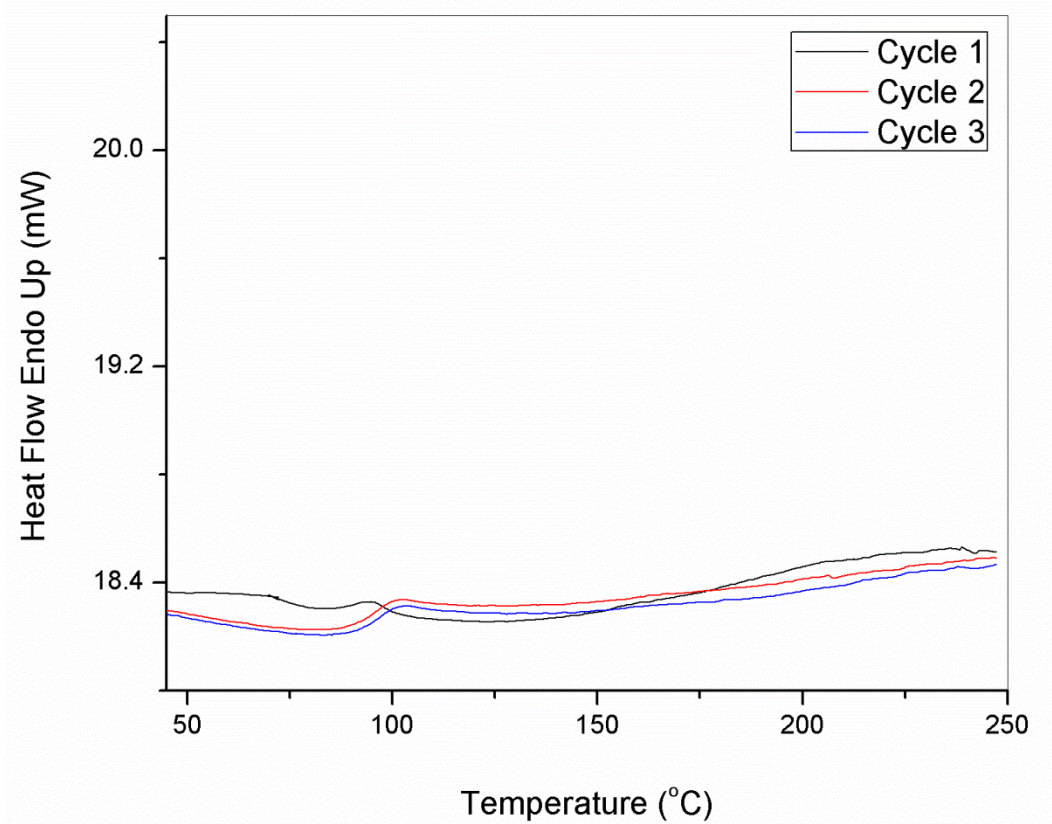


Figure 7.7: DSC thermograms for ACNT GFRP specimen cured for 10 h at 85°C

7.3.1.1 Effect of optimal curing schedule on mechanical behavior of ACNT GFRP

The mechanical performance of the ACNT GFRP samples prepared with 3 different curing conditions (as stated above) have been compared vis-à-vis samples cured for 7h at 70°C (referred to as ‘Reference’ sample) in Figures 7.8 and 7.9.

Interestingly by altering the curing schedule, the mechanical test results have shown significant enhancement in matrix-dominated properties i.e. tensile modulus and strength. The maximum improvement of 48%, 30% and 10% in tensile modulus, strength, and flexural modulus respectively, was witnessed for ACNT GFRP composites cured for 7h at 85°C as compared to the reference sample properties (refer to Figures 7.8 and 7.9). From the above discussion, it is evident that the thermal and mechanical behavior of composites cured for 7h at 85°C has scored over the other two curing schedules i.e. 10h at 70°C and 10h at 85°C.

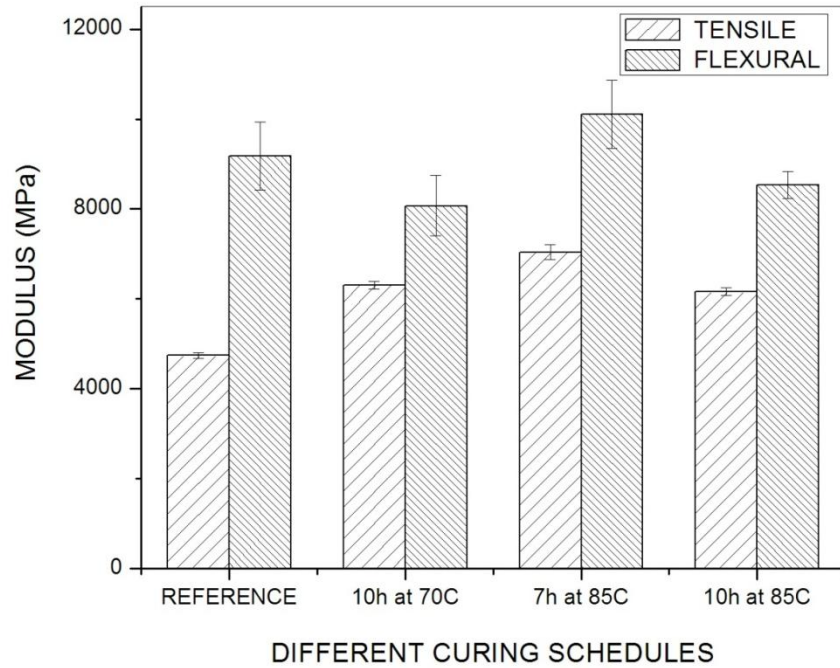


Figure 7.8: Behavior of ACNT GFRP samples with varying curing schedules- Modulus

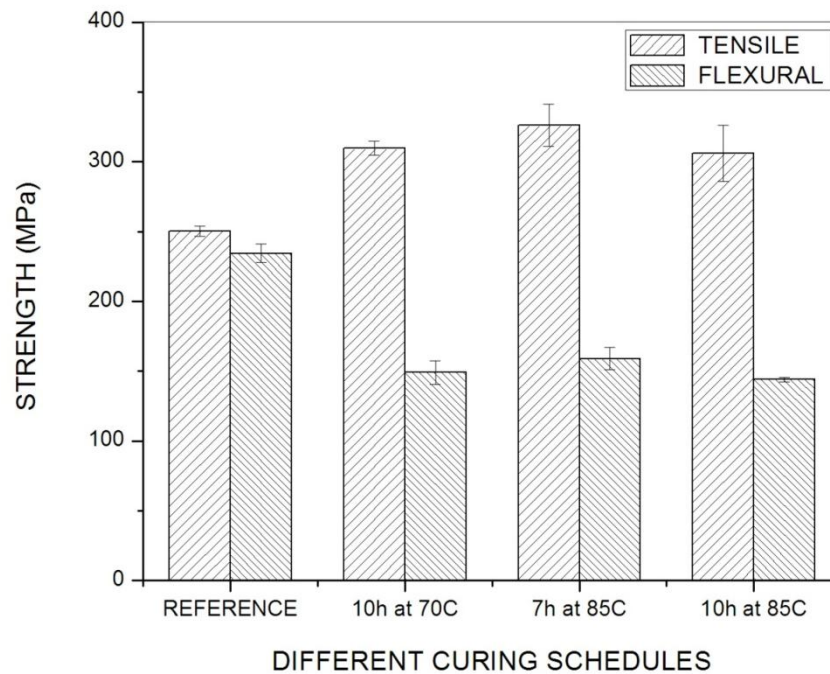


Figure 7.9: Behavior of ACNT GFRP samples with varying curing schedules- Strength

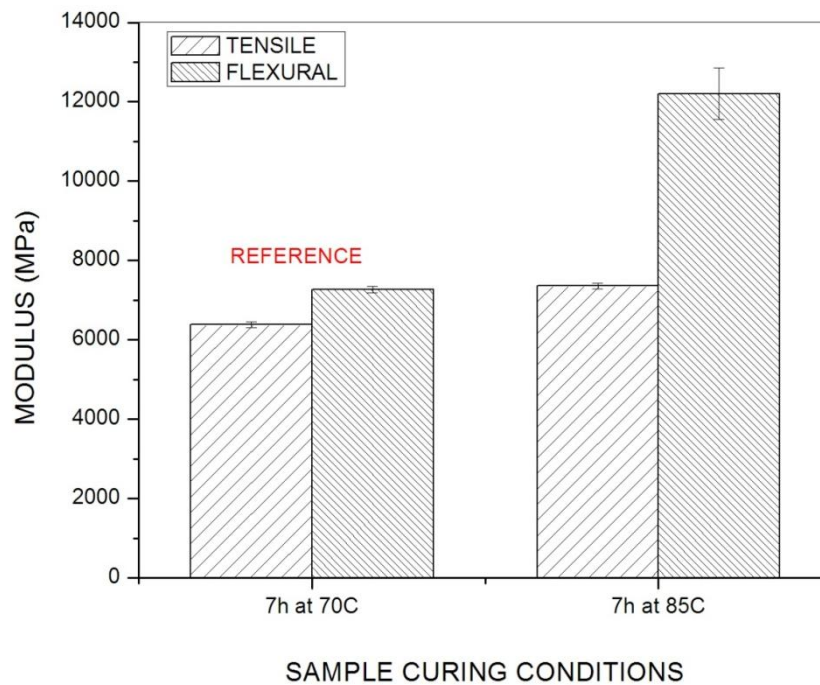
Therefore, after taking into consideration the findings from the thermal and mechanical analysis, it may be concluded that by following the 7h at 85°C curing schedule, ACNT GFRP samples became fully cured and subsequently enhanced the fibre-matrix interfacial adhesion as witnessed by noteworthy increase in mechanical properties. Thus, a curing schedule of 7 h at 85°C has been selected as the optimal curing schedule for such systems and implemented in the preparation of other samples in the present study.

7.3.2 Effect of implementing optimal curing schedule on different GFRP compositions

7.3.2.1 EP GFRP composition

EP GFRP laminates were again prepared by taking into account the optimal curing schedule determined experimentally (as discussed in Section 7.3.1) and tested under both tensile and flexural loading modes to examine the effect on the composite properties. The mechanical properties obtained after following the optimal curing schedule (for 7h at 85°C) were compared to samples (of the same composition) prepared according to supplier's curing schedule (for 7h at 70°C) and are illustrated in Figure 7.10 (a and b).

(a)



(b)

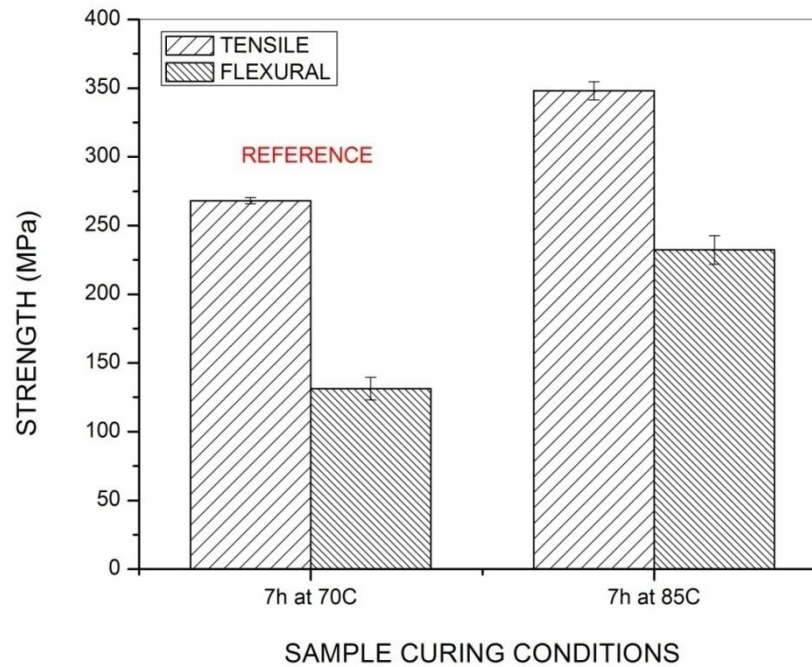
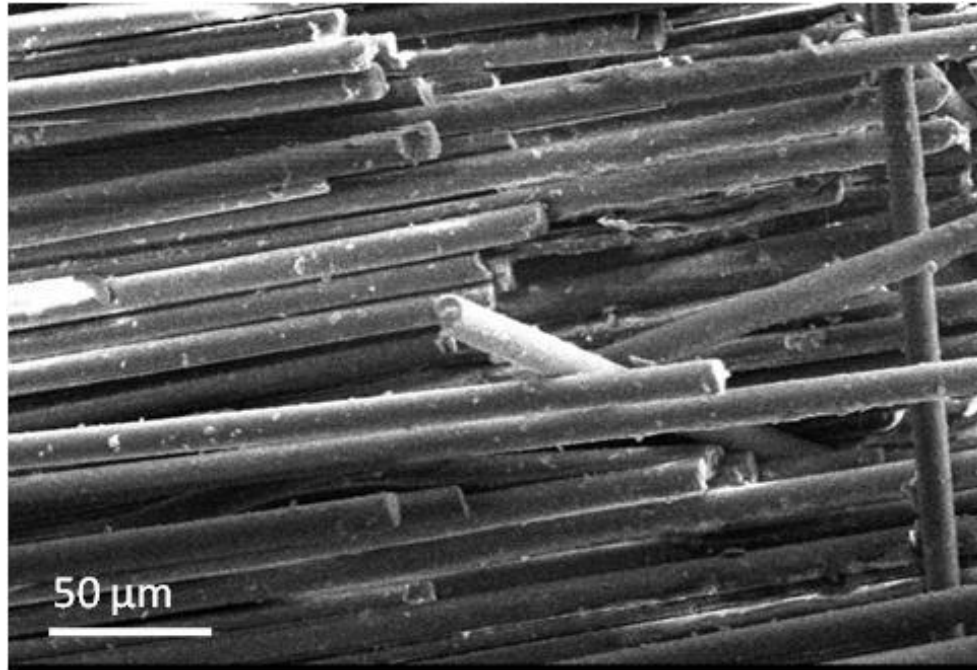


Figure 7.10: Effect of optimal curing conditions on EP GFRP composition (a) Modulus, (b) Strength

It is quite evident from Figure 7.10a, that the stiffness of the composites are slightly affected by modifying the curing schedule of EP GFRP composites. This is due to the fact that this composition did not have any nano-fillers embedded in the epoxy matrix. On the other hand, tensile strength has shown an increase of 30%, which suggests an improvement in interfacial adhesion between the fibres and the matrix due to the additional thermal energy provided by increasing the curing temperature. Furthermore, it is observed that flexural modulus increased by 68% (refer to Figure 7.10a) while the strength by 77% (refer to Figure 7.10b) as compared to the reference sample. The increase in flexural properties strongly supports the strong fibre-matrix interfacial bonding probably due to proper wetting of glass fibres and also the additional thermal energy in the polymer matrix molecules, which allows them to form bonds with the maximum fibre surface prior to its complete gelling. In addition to this, Figure 7.11 compares the morphology of the samples prepared according to supplier curing schedule to that with optimal curing schedule. It is interesting to observe that an increase in the curing temperature demonstrates (refer to Figure 7.11b) better wetting, less fibre breakage or delamination as well as

fibre plies are completely surrounded by the epoxy matrix thus validating the strong interfacial adhesion between them.

(a)



(b)

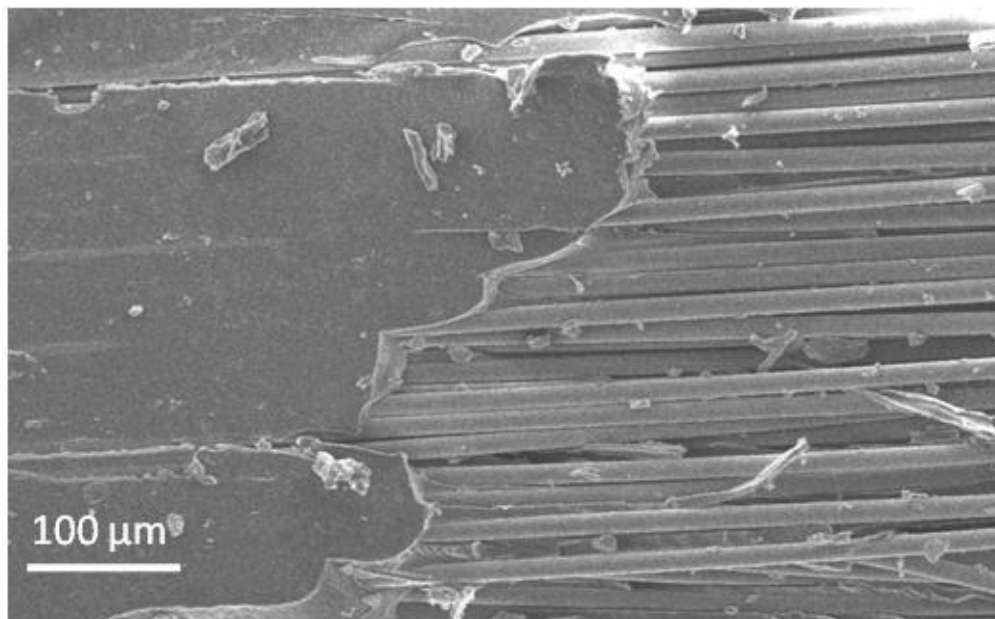
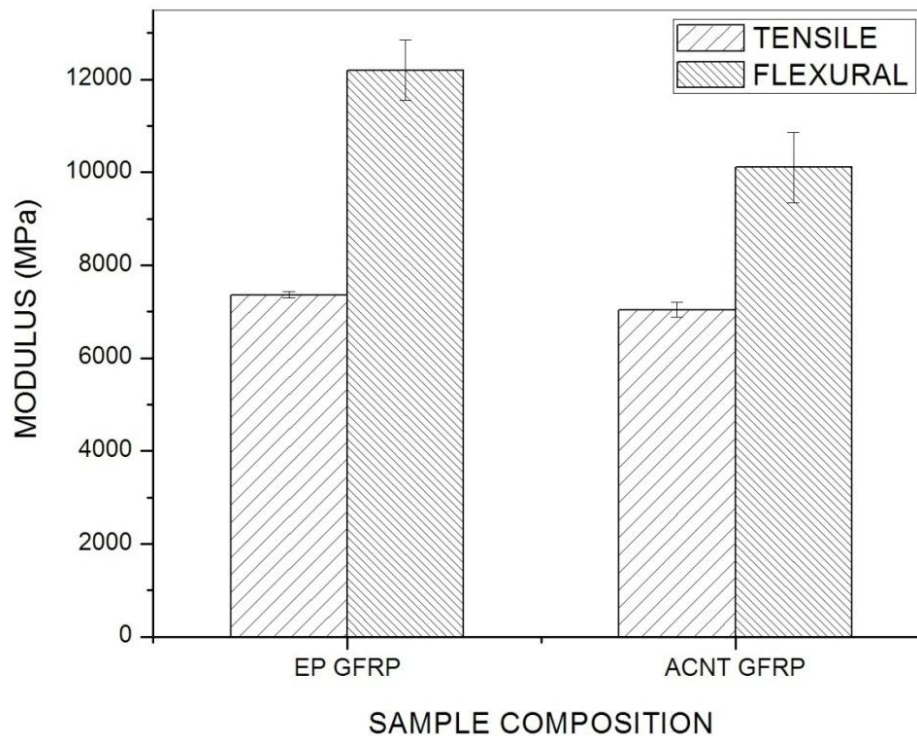


Figure 7.11 : Morphology of EP GFRP composite cured for (a) 7h at 70°C (b) 7h at 85°C

Therefore, the results obtained so far clearly demonstrate significant improvement in mechanical properties on modifying the curing schedule as witnessed for EP GFRP, and ACNT GFRP composites.

Additionally, a comparison of tensile and flexural properties of EP GFRP and ACNT GFRP specimens when cured using optimal curing schedule is illustrated in Figure 7.12 (a and b). The graphs depict no change in tensile modulus and strength with the addition of ACNT whereas, the flexural modulus and strength plunge. A possible reason that explains the deterioration in flexural properties is due to the inefficient stress transfer from the matrix to nanotubes. It is known that the addition of CNTs in epoxy resin increases the viscosity of the mixture and occurrence of voids which indirectly affects the interfacial adhesion. However, to further improve the interaction between epoxy matrix and glass fibres, surface treatment of fibres with silane coupling agents has been done and significant improvement in flexural properties has been observed as reported in our previous study [Garg *et al.*, 2016]. The influence of silane treatment of glass fibres on the properties of ACNT GFRP composites has been discussed in the section ahead.

(a)



(b)

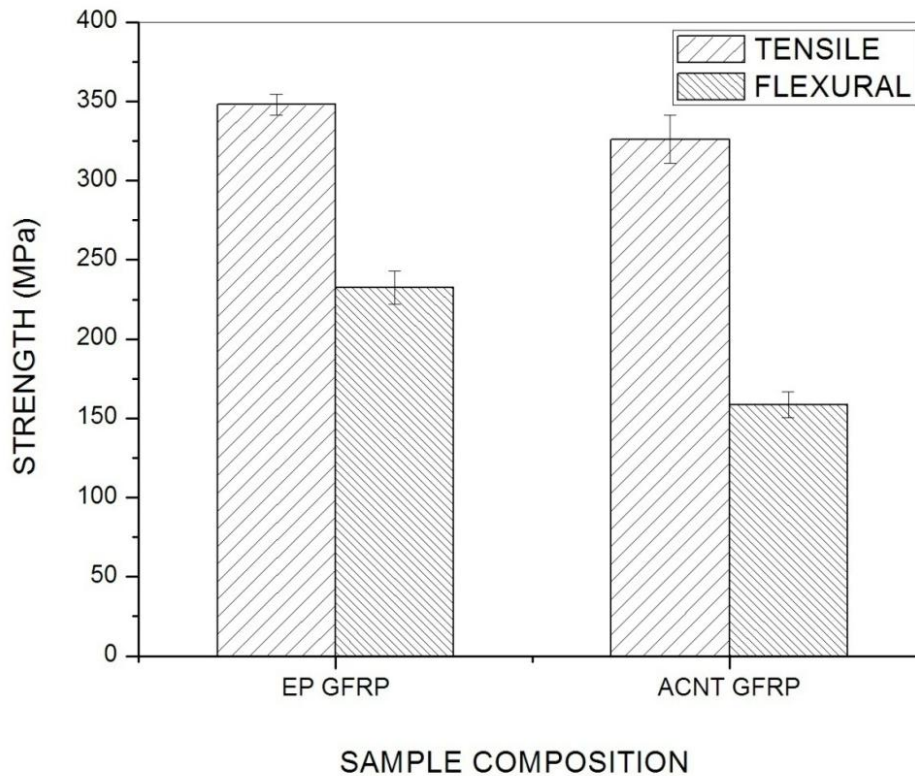


Figure 7.12: Comparison between EP GFRP and ACNT GFRP for optimal curing conditions (a) Modulus, (b) Strength

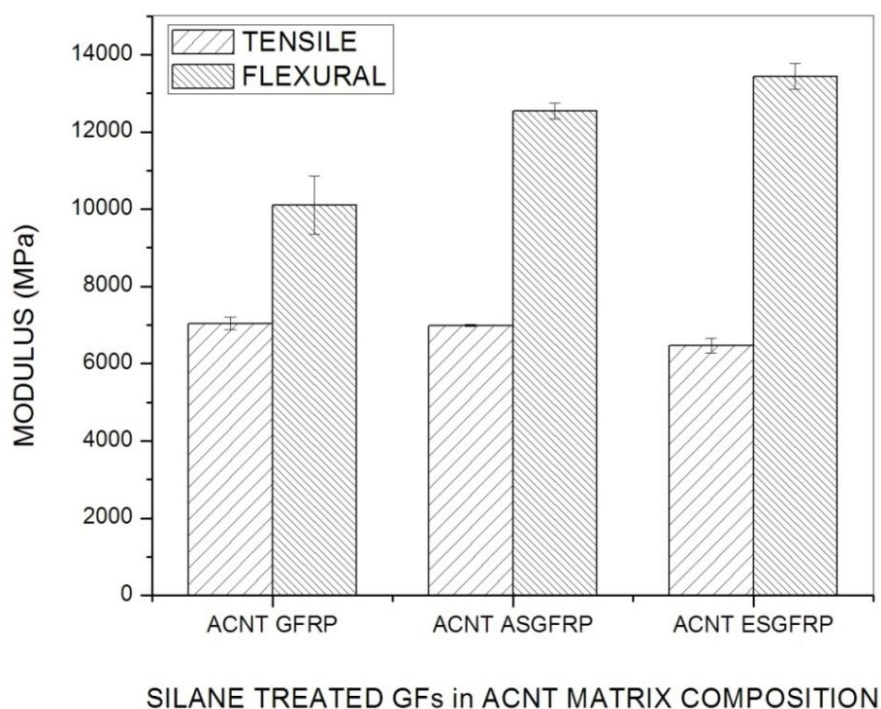
7.3.2.2 Effect of silane treatment of glass fibres in ACNT and PCNT matrix composition

The results reported in Section 7.3.1 showed considerable enhancement in tensile and flexural properties of ACNT GFRP composites prepared by using optimal curing schedule. To extend it further, in this section, the effect of treating the glass fibre mat with silane coupling agents is presented while following the optimal curing conditions and similar matrix composition. Thus, the glass fibre mats were treated with either amino silane (AS) coupling or epoxy silane (ES) coupling agents which would further enhance the fibre-matrix interaction during its fabrication phase. It is known that the silane treatment makes the fibre surface chemically active as functional groups such as epoxide or amino are deposited on the surface, which further interact with the resin mixture during manufacturing in VARIM. The possible chemical interactions between epoxy, amino-CNTs, silane treated glass fibres and amine hardener has been illustrated by a schematic diagram shown in Figure 4.3 (of Chapter 4). From

the figure it is quite evident that epoxide groups of silane agents will tend to form covalent bonds with either amino functionalized nanotubes (ACNT) or with the amine hardener due to opposite polarity and thus form strong covalent linkages. Similarly, the amino groups present on the fibre surface will possibly form a strong bond with the resin epoxide groups thus improving the fibre-matrix interfacial adhesion.

In order to evaluate the performance of silane treated glass fibres in ACNT matrix composition, samples were prepared following the optimal curing schedule and silane treatment procedure (as detailed in Section 4.2.2.2 and 4.2.2.3). Performance of epoxy silane (ESGFRP) and amino silane treated (ASGFRP) samples were carried out under both tensile and flexural modes and compared to ACNT GFRP samples (as-received glass fibres) as shown in Figure 7.13 (a and b). Evidently from Figure 7.13, it can be stated that flexural properties (being fibre-dominated) have scored over tensile properties. The glass fibre surface was modified by silane treatment, thus, resulting in strong covalent bonding with the epoxy matrix as hypothesized. Particularly, flexural modulus increased by 24% and 33% for ASGFRP and ESGFRP, respectively vis-à-vis ACNT GFRP samples.

(a)



(b)

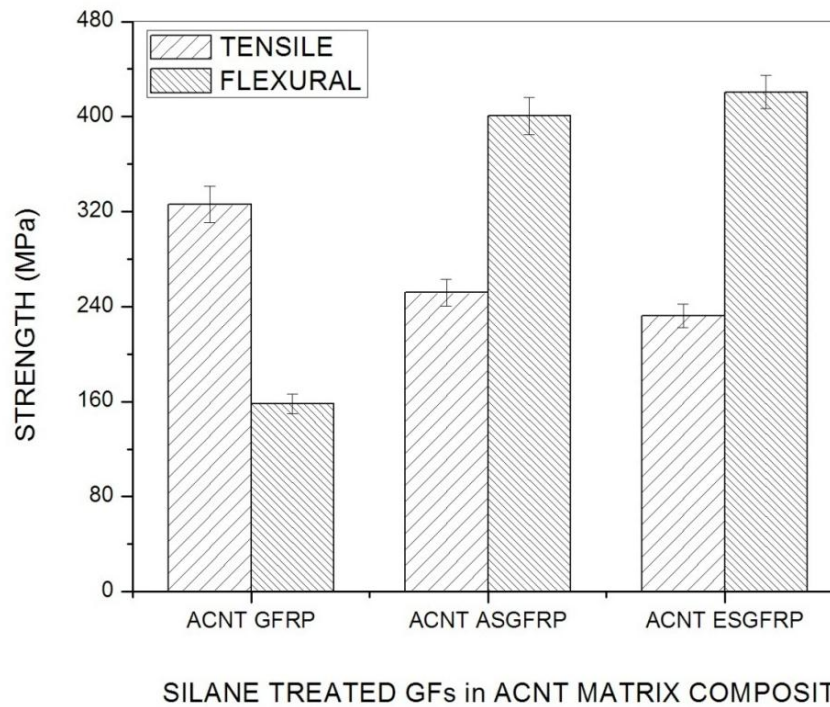


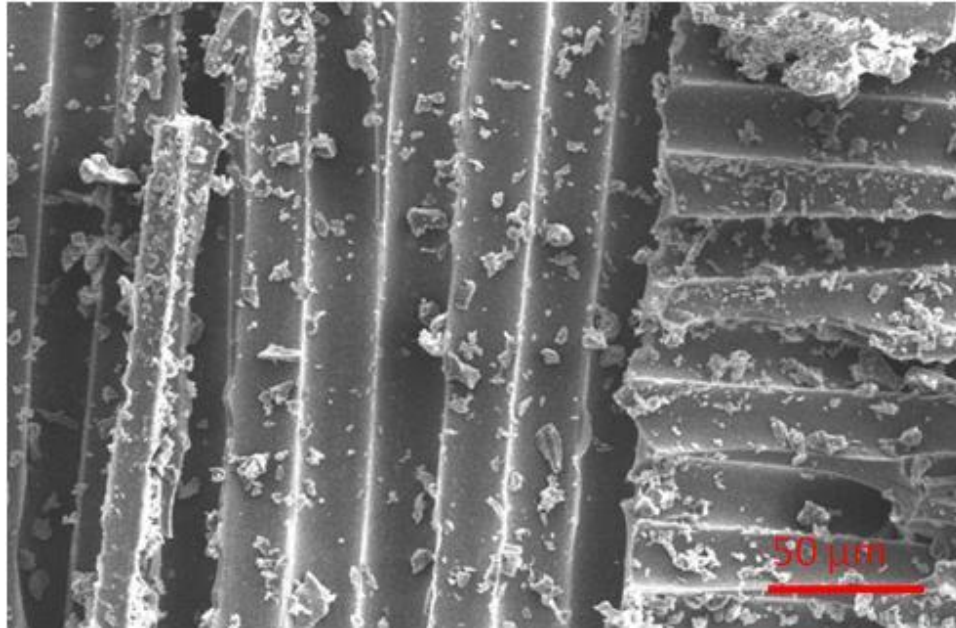
Figure 7.13: Effect of optimal curing conditions on silane treated glass fibres in ACNT matrix: (a) Modulus, (b) Strength

Similarly, flexural strength demonstrated a noteworthy increase, 153% for ASGFRP and 166% for ESGFRP, as compared to the ACNT GFRP sample which had strength of 158 MPa when prepared under the same conditions. It is also important to point out that silane treatment of glass fibres did not affect the stiffness of the composite material under tensile mode.

Figure 7.14 presents the morphology of the two samples and it can be stated that for ES samples (Figure 7.14a), a clear glass fibre surface with small particle depositions of matrix cracking and clusters of epoxy silane agent was visible whereas, a strongly bonded interconnected network along with a layer of matrix bonded to the fibres was seen for AS treated samples (Figure 7.14b). Additionally, the reinforcement of amino silane glass fibres in an ACNT epoxy matrix, illustrates slightly higher tensile modulus and strength as compared to ACNT ESGFRP samples. Also the flexural properties of ACNT ASGFRP specimens show significant improvement when compared to ACNT GFRP specimens, but, it is slightly lower than ACNT ESGFRP sample. Ignoring the minute difference between the flexural properties of amino silane

and epoxy silane it may be stated that an overall assessment of both flexural and tensile properties demonstrates better performance by ACNT ASGFRP composite.

(a)



(b)

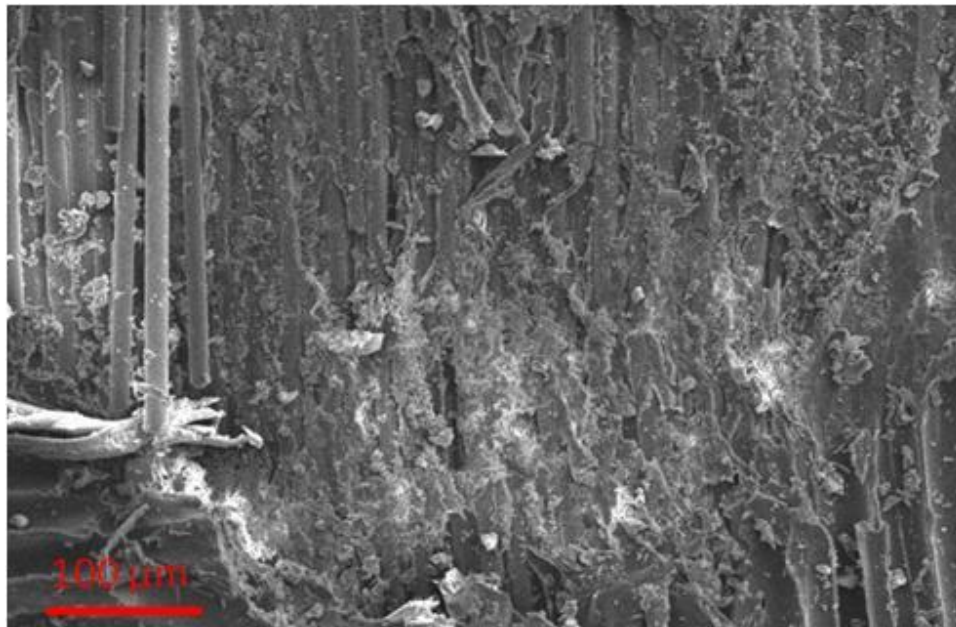


Figure 7.14: Morphology of ACNT (a) ESGFRP and (b) ASGFRP samples cured for 7h at 85°C

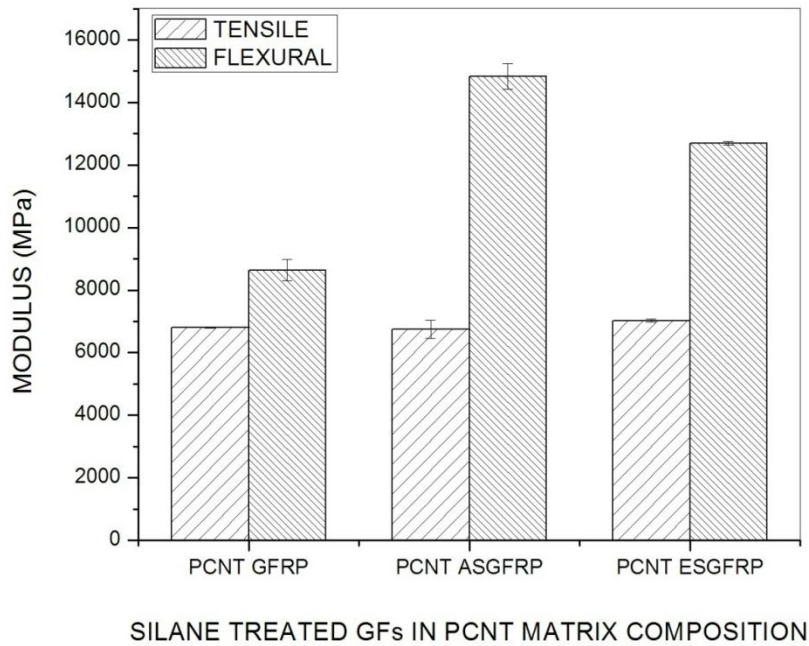
The results validate the improved fibre-matrix interface which is due to strong covalent bonding between active functional groups on glass fibres with amino-CNTs and with the hardener formed during fabrication in VARIM as also revealed by a thick layer of amino silane strongly adhered on the fibre surface (as shown in Figure 7.14b). Following this, it became interesting to analyze if a similar effect of fibre surface treatment was also possible when the epoxy matrix was reinforced with pristine nanotubes (PCNT) while, keeping the processing conditions same and following the optimal curing schedule as done previously for ACNT composition.

It is worthy to mention that in our previous study, the polymer nanocomposites fabricated using PCNT had shown enhancement in mechanical properties vis-à-vis EP GFRP and ACNT GFRP composites [Garg *et al.*, 2015]. However, considering the optimal curing schedule determined experimentally in this study, PCNT GFRP composites were again manufactured and mechanically tested. A comparative analysis between EP GFRP and PCNT GFRP samples was carried out and it was observed that the stiffness (tensile modulus) of the matrix was slightly affected by the addition of PCNT in an epoxy matrix. Additionally, the remaining mechanical properties (tensile strength, flexural strength, and modulus) also showed lower values as compared to EP GFRP sample. Such behavior is due to the lack of strong covalent bonding between the modified resin and the glass fibres, owing to the lack of active functional groups on the sidewalls of pristine nanotubes as compared to ACNT. In addition to this, the use of PCNT facilitates the crosslinking at initial curing period, but tends to lower the enthalpy peak temperature, which in turn prevents the occurrence of vitrification and thus lowers the T_g as compared to EP GFRP composite [Zhou T. *et al.*, 2009]. Further the aim of the present study was to examine the impact of fibre surface treatment when manufactured in PCNT modified epoxy matrix composition and the same has been discussed ahead.

As reported earlier for ACNT GFRP composition, samples were prepared with glass fibres treated with either AS or ES and then infused with CNT/Epoxy mixture (i.e. an epoxy mixture with pristine nanotubes) in VARIM while, following the optimal curing schedule. The fabricated PCNT ASGFRP and PCNT ESGFRP specimens were also subjected to tensile and flexural tests. The experimental results obtained have been shown in Figure 7.15 (a and b) along

with the results of control sample i.e. PCNT GFRP (AR GF) prepared with the optimal curing schedule.

(a)



(b)

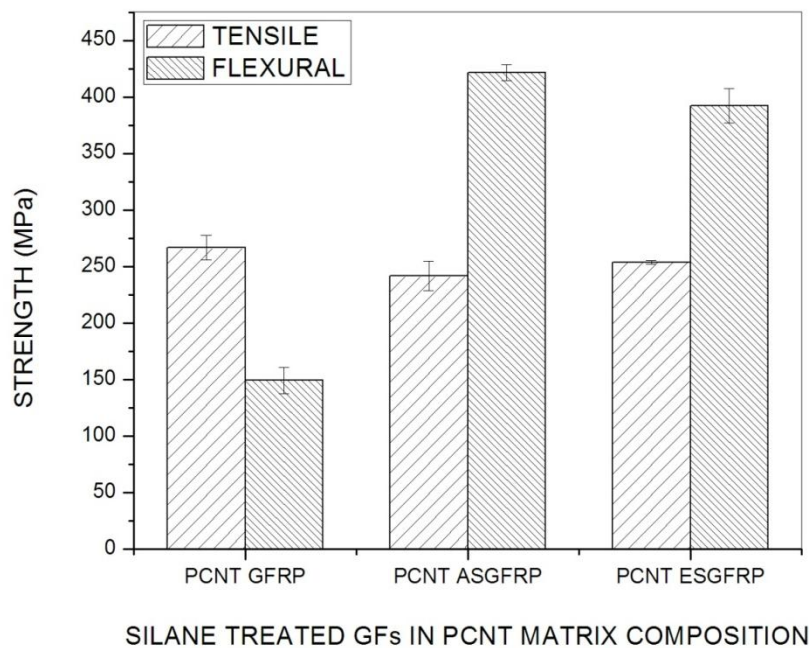


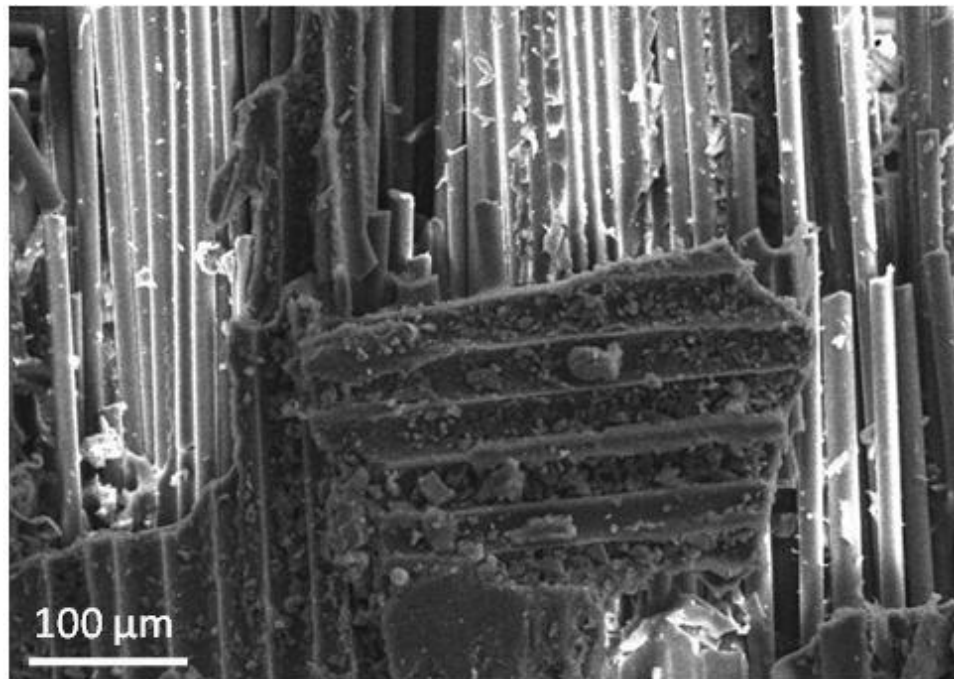
Figure 7.15: Effect of optimal curing conditions on silane treated glass fibres in PCNT matrix: (a) Modulus, (b) Strength

Once again, the stiffness of the samples remain unaffected by treating the glass fibres with amino and epoxy silane coupling agents (refer to Figure 7.15a). On the other hand, with PCNT matrix composition, the tensile strength dropped by about 9% and 5% for AS and ES treatments, respectively. Hence, it may be stated that the tensile properties show better results for PCNT ESGFRP composition. Also, the drop in tensile strength for PCNT silane treated GFRP samples is relatively less than what was observed for ACNT GFRP samples. Further, having an insight of flexural properties depicted in Figure 7.15 (a and b) it may be observed that (i) the value of flexural modulus i.e. 14.8 GPa was recorded for PCNT ASGFRP and 12.7 GPa for PCNT ESGFRP compositions, respectively, as compared 8.6 GPa for the control sample, (ii) the flexural strength showed an excellent behavior i.e. an improvement by 180% and 160% in PCNT ASGFRP and PCNT ESGFRP composites, respectively vis-à-vis the PCNT GFRP composition. Although, the PCNT ASGFRP shows slightly better flexural properties as compared to PCNT ESGFRP, but the same may be neglected on the basis of very small difference as well as weak behavior observed in the tensile properties. Thus, it may be concluded that as compared to the control sample (PCNT GFRP), PCNT ESGFRP composites show an overall acceptable performance.

On comparing the morphology of epoxy and amino silane treatments for PCNT matrix composition, it can be observed in Figure 7.16a that ESGFRP sample shows (i) more rough surface, due to particle deposition, (ii) glass fibre sheets are embedded in the matrix and (iii) crack propagation was possibly through the matrix rather than the fibres. On the other hand, ASGFRP sample (refer to Figure 7.16b) illustrates lesser deposition on fibre surface along with small granules of broken fibre between the individual fibre strands. Thus, the morphological analysis along with mechanical properties supports the existence of better fibre-matrix interface for ESGFRP samples over ASGFRP.

Results from Figures 7.13 and 7.15 highlight the fact that, the presence of excess amino groups during the curing of the composite plays an important role. This is because, it tends to further accelerate the curing reaction and builds inter-crosslinking network between the amino silane treated glass fibres and epoxide of resin.

(a)



(b)

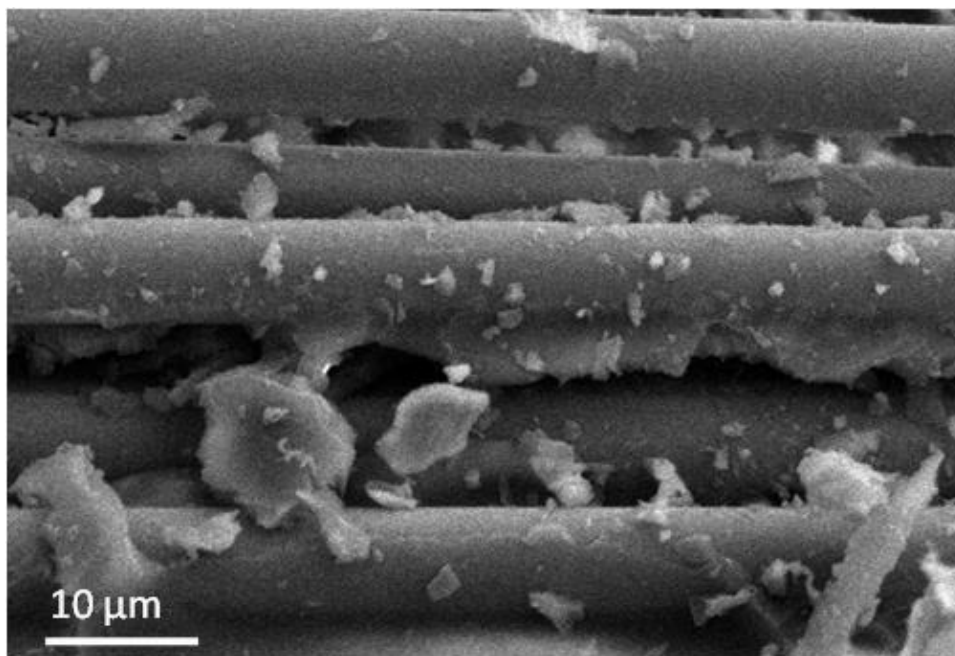


Figure 7.16: Morphology of PCNT (a) ESGFRP and (b) ASGFRP samples cured for 7h at 85°C

Therefore, from the above analysis, it can positively be stated that the addition of amino functionalized nanotubes in epoxy resin alters the curing behavior and also forms a strong, long cross-linked polymer chain with fully cured matrix at the end of the manufacturing process as well as form strong covalent linkages with the glass fibre sheets. Interestingly, the observations drawn from the results of this chapter are consistent with our earlier work (refer to Chapter 4) where, the processing of functionalized and pristine carbon nanotube epoxy composites with silane treated glass fibre was examined for the samples prepared according to suppliers curing schedule.

7.4 Closing remarks

In the chapter, an attempt was made to study the curing behavior of CNT reinforced composites and it was found from thermal analysis that, there was still some uncured epoxy resin left, which would tend to attract and retain water molecules during exposure to sea water for e.g. in naval applications. As a result, optimal curing schedule, i.e. for 7h at 85°C was obtained experimentally. Following which, the ACNT GFRP samples illustrated the absence of enthalpy relaxation peak in DSC thermograms and showed 48% and 30% improvement in tensile modulus and strength, respectively. Besides, the amino silane treated glass fibres in ACNT composition revealed an enhancement by 153% in flexural strength. Similarly, PCNT GFRP samples reinforced with epoxy silane fibres demonstrated an improvement of 160% in flexural strength as compared to their respective samples prepared with as-received glass fibres. Interestingly, the outstanding results obtained for silane treated fibres with nanotubes were consistent with our earlier work where the samples were prepared according to suppliers curing schedule.

Chapter 8. Conclusion and Recommendations for future work

This research study reports the key findings of reinforcing EP GFRP composites with functionalized and pristine nanotubes with respect to its mechanical and hygrothermal performance. Also, it has opened new horizons for preparing FRP modified polymer composites having wide applicability in marine environment along with the damage detection during their in-service, submerged conditions. A comprehensive understanding of composition-processing-structure-property in these systems has been achieved.

8.1 CNT modified GFRP composites

1. The combination of sonication and high shear homogenization processing techniques is as an effective methodology to attain uniform and homogeneous dispersion of carbon nanotubes in an epoxy matrix at a low loading level. The dispersion of amino-functionalized nanotubes (ACNT) in an epoxy resin demonstrated a better and stable dispersion as well as strong interfacial adhesion developed during the pre-curing phase of manufacturing glass fibre composites in VARIM as compared to dispersion of PCNT in epoxy resin. Furthermore, considerable improvement in mechanical properties was seen for EP GFRP samples with resin infusion temperature more than 40°C as compared to supplier's recommendation i.e. 25°C. Increase in temperature lowered the viscosity of the resin mixture which aided in better dispersion of CNTs in the epoxy matrix, good wettability of the mixture with glass fibre mat, reduced porosity and CNT agglomerates in the composite interface.
2. For the first time, the present study reported higher mechanical behavior for the composites with pristine nanotubes (PCNT) reinforcement in epoxy resin as compared to those with ACNT at stoichiometric ratio. The improvement was 26% in tensile modulus, 42% in tensile strength, 50% in flexural modulus and 74% in flexural strength as compared to EP GFRP sample.
3. On the other hand by altering the stoichiometric ratio, i.e. amine-rich resin system, ACNT GFRP composites demonstrated significant enhancement in mechanical properties, i.e. an increase in tensile modulus by 39%, tensile strength by 38% and

flexural modulus by 43% and flexural strength by 95% as compared to the EP GFRP sample prepared with stoichiometric ratio. The enhanced properties of ACNT in amine-rich resin system is possibly due to the highly cross-linked network built between the ACNTs and the epoxide group of resin during the early curing stage which was minimal in the case of pristine CNT. The stronger interfacial bonding with the matrix and efficient stress transfer from the matrix to CNTs resulted in improved mechanical properties.

4. Characterization techniques such as TEM and SEM have also confirmed the formation of chemical bonds between the epoxy resin, CNTs and glass fibre mat. Especially, the CNT-bridging mechanism in the crack propagation regions as observed in SEM images verified the strong bonding amongst amino-CNT, epoxy matrix and the glass fibre. Furthermore, FTIR spectrums of the ACNT GFRP and EP GFRP composites were in good agreement with the chemical reactions occurring between the nanotubes and the matrix that were further correlated with improved mechanical properties.

8.2 Silane treatment of glass fibres

To further enhance the strengthening of fibre-matrix interface, glass fibre surface were treated with epoxy and amino silane coupling agents. These treated fibres were then used to prepare multifunctional composite laminates by infusing neat epoxy or CNT/Epoxy mixture (both ACNT and PCNT) in VARIM.

1. Epoxy and amino silane treatment of glass fibres significantly enhanced the flexural properties in EP GFRP composition. Heat-treatment prior to the silanization also showed a positive effect on the mechanical behavior.
2. Furthermore, CNT reinforced silane treated glass fibre composites exhibited a complex stress-transfer mechanism. Specifically, ACNT ASGFRP composites exhibited enhanced mechanical behavior, possibly due to the formation of 3-D cross linked network and CNT-bridging mechanism observed between ACNT/Epoxy matrix and amino silane glass fibre. The SEM images of fractured surfaces of these composites did not indicate any fibre pullouts, thus signifying good interfacial adhesion among them. Additionally, CNT-bridging mechanism in the crack propagation regions further confirm the existence of strong bonds between amino-CNT, epoxy matrix and the glass fibre.

3. On the other hand, PCNT composites showed appreciable improvement in mechanical properties when fabricated with epoxy silane coupling agent. In general, the surface treatment of glass fibres transformed the failure mode of composites from ductile to brittle.
4. Moreover, the reinforcement of ACNT in the hardener instead of resin showed fewer CNT agglomerates and the mechanical properties improved by more than 30% for tensile and around 10% for flexural loading conditions.
5. Lastly, a composite was prepared in which 0.1 wt% ACNT was uniformly dispersed in an amine-rich epoxy resin by implementing sonication and high-shear homogenization techniques along with higher CNT/resin infusion temperature. The final mixture was then infused into the amino silane treated glass fibres for fabrication. Mechanical test results of ACNT ASGFRP (amine-rich resin composition) revealed more than 95% improvement in flexural strength and about 8% for tensile strength as compared to EP GFRP sample.

8.3 Hygrothermal aging

The diffusion and mechanical behavior of various GFRP composites fabricated, was examined after exposure to hygrothermal conditions (in seawater (SW) and distilled water (DW)) both in warm (55°C) and ambient (25°C) temperatures.

1. The kinetics of water diffusivity results reveal that water absorption during the initial stages follows Fickian behavior, but with prolonged aging a different trend has been observed which is being reported for the first time. Interestingly, the maximum or equilibrium water content and the diffusion coefficient values were smaller for hybrid composites vis-à-vis GFRP composites when exposed to same SW and DW environments, possibly due to the hydrophobicity (for PCNT), and high barrier properties of CNTs. Additionally, the percent weight gain reported for GFRP composites due to water absorption is found to be higher in DW as compared to SW aging conditions. A possible chemical and interface mechanism has been proposed, which explains the increase in water uptake in composites after exposure to seawater for longer durations.

2. Interestingly, a decrease in mechanical properties was observed initially, however at a later stage the trend reversed and a recovery in the mechanical properties was clearly seen for both EP GFRP and ACNT GFRP samples. This recovery in mechanical properties is ascribed to the possible secondary crosslinking network between excess sodium ions in seawater with the hydroxyl groups of cured epoxy and also to the unreacted silanols on the glass fibre surface. FTIR and SEM images support the observations made using mechanical tests for EP GFRP samples after exposure to the hygrothermal aging environment. SEM images along with EDS spectra have confirmed the diffusion of seawater into the fibre-matrix interface and various damages onto the fibre surface.
3. On the contrary, PCNT GFRP composites exhibited a continuous decreasing trend in stiffness, strength, and elongation at break properties with increase in aging time. Interestingly, PCNT samples exhibited similar values as ACNT for stiffness, strength, and strain at break after 121 days of aging in SW. But, considering the percent change in all flexural properties, the recovery mechanism and morphology observed for ACNT samples, it can be stated that in hygrothermal environment the ACNT GFRP samples outperform.
4. The double edge coating of EP GFRP and ACNT GFRP samples revealed a considerable decrease in % weight gain and D values as expected, but, their mechanical properties showed an even further drop as compared to single edge coated samples.
5. Further, the exposure of all the composites at an elevated temperature resulted in quantitatively higher water uptake content, followed by a steep fall in strength, stiffness and elongation at break.
6. Lastly, it was observed that a thin silane layer provided better protection to the fibre surface as it resisted the harsh effect of absorbed seawater. Overall the presence of a silane layer on fibre surface demonstrated better hygrothermal performance as compared to ACNT GFRP composites in identical environment conditions.

One interesting observation from the experimental results is the possibility of pre-conditioning by immersing the components made of these nanocomposites in SW for a few days (15-20 days) before being installed, for e.g., in a ship, so that significant recovery of properties takes place.

This will prevent the initial steep drop in properties which would take place, otherwise at very high loading.

8.4 Damage monitoring in GFRP laminates

The defects or damages introduced in the composites during in-service conditions such as exposure to marine environment results in the form of notches, material degradation, surface discontinuities, etc. that needed to be monitored prior to the failure of structural components. One of the major requirements was to develop a damage monitoring methodology which could efficiently monitor these defects without being removed from their current assemblies. As a result, by using a pair of mobile immersion probes, specific Lamb wave modes were generated and examined both manufacturing defects and usage damages in EP GFRP sheets under submerged conditions.

1. In the present study, the efficacy of ultrasonic guided waves in submerged composite laminates was established which was non-contact, *in-situ* and non-invasive technique to detect the damages and quantify their severity. Experimentally, specific Lamb waves were excited by controlling various parameters of the ultrasonic setup. An ultrasonic signal with good fidelity was recorded over the healthy regions and considered as a baseline for damage detection.
2. Lamb waves were successful in picking up manufacturing defects such as air gaps and missing epoxy in the prepared EP GFRP sheets. The transmitted signal strength falls when the Lamb wave interacts with these defects. Interestingly, the sharpness and time of flight of the received signal remain unaffected by the presence of these defects in EP GFRPs.
3. Also, the Lamb waves were sensitive to degradation in the EP GFRP laminates due to its continual usage causing defects like notches, material degradation, surface discontinuities, etc. The fall in voltage amplitude is an indicator of these defects in EP GFRP sheets while in-service. Thus, Ultrasonic guided waves were sensitive to both internal and external defects in two-ply GFRP composites and this characteristic can be exploited as an effective damage monitoring technique for other purposes.

4. Further an attempt was made to correlate the drop in mechanical properties with the corresponding ultrasonic signal strength of EP GFRP samples, conditioned in SW for varying immersion times. In general, mechanical properties showed a decreasing trend as immersion time increased. A reduction of 48% in strain and 66% in the tensile strength were observed after a period of 60 days immersion in SW conditions. The overall degradation in the properties is mainly due to plasticization effect, swelling of the matrix and loss of good interfacial bonding between the glass fibres and the matrix when conditioned for a long time.
5. Similarly, the non-destructive test results also indicated an increasing trend of the percentage drop in signal strength as the duration of specimens in the SW increased. The decrease in peak to peak voltage amplitude is likely due to loss of adhesion or de-bonding at the fibre-matrix interface, moisture absorption, matrix swelling and chemical attack on matrix and fibre which results in greater attenuation of the signal.
6. Lastly, it was observed that the loss in guided wave voltage amplitude correlates well with the decreasing tensile strength and strain to break with increasing time of immersion.
7. Also, the damage monitoring tool developed in this study could evaluate defects in both EP GFRP and CNT GFRPs. The drop in signal strength with CNT modified GFRPs was higher than neat epoxy GFRPs.

Also, these findings and the developed health monitoring tool can serve as an effective method to diagnose the service life of marine vessels while they are in operational mode.

8.5 Optimal curing conditions of CNT GFRP composites

The motivation behind the study carried out in this manuscript was to analyze the optimal curing condition which tends to minimize the uncured polymer chain. The uncured polymer chain attracts and retains water molecules during exposure to sea water for e.g. in naval applications. Curing as specified by the supplier, 7h at 70°C has been analyzed following which the optimal curing conditions were determined. The conclusions drawn are:

1. From thermal analysis, it has been observed that there is a shift of T_g to the right, i.e. higher temperatures for ACNT GFRP as compared to EP GFRP sample. Thermal as well as

mechanical behavior confirmed the optimal curing conditions, i.e. 7 h at 85°C, required for obtaining uniform dispersion and strong interfacial adhesion in CNT/Epoxy nanocomposites.

2. ACNT GFRP nanocomposites fabricated by implementing the optimal curing schedule illustrated the absence of enthalpy relaxation peak in DSC thermograms and showed 48% and 30% improvement in tensile modulus and strength, respectively. Hence, suggesting a maximum curing of resin and an improved stable fibre-matrix interfacial bonding.
3. Implementation of optimal curing schedule significantly enhanced the tensile and flexural properties of EP GFRP composites while; the flexural strength plunged for ACNT GFRP composites.
4. To enhance the fibre-dominated properties, silane treatment showed a positive effect for both ACNT and PCNT GFRP samples. From the overall analysis of mechanical properties it has been observed that ACNT GFRP shows 153% enhancement in flexural strength with AS treated fibres, whereas, PCNT GFRP demonstrated 160% improvement with ES treatment.

On the whole, silanization of glass fibre mat and optimization of the curing schedule has proved to be beneficial with respect to the mechanical performance of CNT modified GFRP composites.

8.6 Future scope of work

1. The present study incorporated reinforcement of GFRP composites with carbon nanotubes at a fixed low weight percentage which could be further increased to study their resulting effect on the mechanical and hygrothermal behavior
2. Studies could be conducted to investigate the effect of the addition of other nano-fillers such as graphene, carbon nanotubes and combinations of these on the strength and stiffness of the nanocomposites.
3. The sensitivity of different guided Lamb wave modes could be investigated for specific defects in composite materials. Also the correlation between the non destructive guided wave parameters and destructive parameters of mechanical testing can be developed to facilitate non destructive evaluation of different types of GFRP composites (neat or modified) during manufacturing and usage.

References

- Abdel-Magid B., Ziaee S., Gass K., Schneider M., "The combined effects of loads, moisture, and temperature on the properties of E-glass/epoxy composites." *Composite Structures*, 71, **2005**: 320-326.
- Abhilash AS, Joshi SP, Mukherjee A., "Micromechanics of diffusion-induced damage evolution in reinforced polymers." *Compos Sci Technol.*, 71, **2011**: 333 - 342.
- Adams R.D., Singh M.M. "The effect of immersion in sea water on the dynamic properties of fibre-reinforced flexibilised epoxy composites." *Composite Structures*, 31, **1995**: 119 - 127.
- Aditya P.K., Sinha P.K., "Diffusion coefficients of polymeric composites subjected to periodic hygrothermal exposures." *J. Reinf. Plast. Compos.*, 11, **1992**: 1035-47.
- Ahmad Z., Ansell M.P., Smedley D., "Moisture absorption characteristics of epoxy based adhesive reinforced with CTBN and ceramic particles for bonded-in-timber connection: Fickian or Non-Fickian behavior." *IOP Conference Series. Materials Science and Engineering*, 17, **2011**.
- Ajayan P.M., Stephan O., Colliex C., Trauth D. "Aligned carbon nanotube arrays formed by cutting a polymer resin nanotube composite." *Science*, 265 (5176), **1994**: 1212 - 1214.
- Aktas L., Hamidi Y., Altan M.C., "Effect of Moisture Absorption on Mechanical Properties of Resin Transfer Molded Composites - Part I: Absorption." *J. Mater. Process. Manuf. Sci.*, 10(4), **2002a**: 239-254.
- Aktas L., Hamidi Y., Altan M.C., "Effect of Moisture Absorption on Mechanical Properties of Resin Transfer Molded Composites - Part II: Desorption." *J. Mater Process. Manuf. Sci.*, 10(4), **2002b**: 255-267.
- Aldajah S., Alawsi G., Rahmaan SA., "Impact of sea and tap water exposure on the durability of GFRP laminates." *Mater Des.*, 30, **2009**: 1835 - 1840.
- Allaoui A., Bounia N. El., "How carbon nanotubes affect the cure kinetics and glass transition temperature of their epoxy composites —A review." *Express Polymer Letters*, 3(9), **2009**: 588-594.
- Anas S., Rehman G. U., Khan Z.M., et al. "Influence of MWCNTs as secondary reinforcement material in glass fiber/epoxy composites fabricated using VARTM." *International Conference on Solid State Physics, ICSSP. Pakistan*, **2013**.
- Ann H.K., Kim M.H., Jhang K.Y., Park I.K., Kwag N.G. "Detection of laser excited Lamb wave using air-coupled transducer and wave mode identification using Wavelet transform." *AIP Conf. Proc.*, 760, **2005**: 1018–1025.
- Apicella A., Nicolais L. "Effect of water on the properties of epoxy matrix and composite. Epoxy Resins Composites I." *Adv. Polym. Ser.*, 72, **1985**: 69-77.
- Arash B., Wang Q., Varadan V.K. "Mechanical properties of nanotube/polymer composites." *Scientific Reports*, 4, **2014**: 6479.

- Arronche L., Gordon K., Ryu D., Saponara V.L., Cheng L. "Investigation of galvanic corrosion between AISI 1018 carbon steel and CFRPs modified with multi-walled carbon nanotubes." *J Mater Sci*, **48**, **2013**: 1315 - 1323.
- Ashrafi B., Guan J., Mirjalili V., Zhang Y., Chun L., Hubert P., Simard B., Kingston C.T., Bourne O., Johnston A. "Enhancement of mechanical performance of epoxy/carbon fiber laminate composites using single-walled carbon nanotubes." *Composites Science and Technology*, **71**, **2011**: 1569-1578.
- Ayatollahi MR, Shadlou S, Shokrieh MM. "Mixed mode brittle failure in epoxy/multi-walled carbon nanotube nanocomposites." *Eng. Fract. Mech.* **78**, **2011**: 2620-32.
- Badcock R.A., Birt E.A. "The use of 0-3 piezocomposite embedded Lamb wave sensors for detection of damage in advanced fibre composites." *Smart Materials and Structures*, **9**, **2000**: 291 - 297.
- Bae J., Jang J., Yoon S.H.,. "Cure behavior of the liquid-crystalline epoxy/carbon nanotube system and the effect of surface treatment of carbon fillers on cure reaction." *Macromol Chem Phys.*, Vol. **203**, **2002**: 2196-2204.
- Bagheri A., Rizzo P. "Guided ultrasonic wave testing of an immersed plate with hidden defects." *Optical Engineering*, **55**(1), **2016**: 011003-011003.
- Baljinder K.K., Bhaskar B., Dennis P., Horrocks R.A. "Studies on the effect of different levels of toughener and flame retardants on thermal stability of epoxy resins." *Polymer Degradation and Stability*, **95**, **2010**: 144 - 152.
- Barkoula N.M., Paipetis A., Matikas T., Vavouliotis A., Karapappas P., Kostopoulos V. "Environmental degradation of carbon nanotube-modified composite laminates: A study of electrical resistivity." *Mechanics of Composite Materials*, **45**(1), **2009**: 21-32.
- Barraza H.J., Aktas L., Hamidi Y.K., Long J., O'Rear E.A., Altan M.C. "Moisture Absorption and Wet-Adhesion properties of Resin Transfer Molded (RTM) Composites containing elastomer coated glass fibers." *J. Adhes. Sci. Technol.*, **17**(2), **2003**: 217-233.
- Bates D., Smith G., Lu D., Hewitt J. "Rapid Thermal Non-Destructive Testing of Aircraft Components." *Composites: Part B*, **31**, **2000**: 175 - 185.
- Baudot C., Tanb CM., Konga JC. "FTIR spectroscopy as a tool for nano-material characterization." *Infrared Phys. Technol*, **53** (6), **2010**: 434 - 438.
- Beg M.D.H., Pickering K.L. "Fiber Pretreatment and Its Effects on Wood Fiber Reinforced Polypropylene Composites." *Materials and Manufacturing Processes*, **21**(3), **2006**: 303-307.
- Bekyarova E., Thostenson E.T., Yu A., Itkis M.E., Fakhrutdinov D., Chou T.W. "Functionalized single-walled nanotubes for carbon fiber-epoxy composites." *J Phys Chem C*, **111**(48), **2007a**: 17865-17871.
- Bekyarova E., Thostenson E.T., Yu A., Kim H., Gao J., Tang J., Hahn H. T., Chou T.W. , Itkis M. E., Haddon R. C. "Multiscale Carbon Nanotube-Carbon Fiber Reinforcement for Advanced Epoxy Composites." *Journal of Langmuir*, **23**(7), **2007b**: 3970–3974.
- Ben B.S., Ben B.A., Vikram K.A., Yang S.H. "Damage identification in composite materials using ultrasonic based Lamb wave method." *Measurement*, **46**, **2013**: 904 - 912.

- Ben B.S., Ben B.A., Kweon S.H., Yang S.H. "Structural Damping of Composite Materials Using Combined FE and Lamb Wave Method." *Structural Engineering and Mechanics*, 51(6), **2014**: 1047-1065.
- Benammar A., Draï R., Guessoum A. "Detection of delamination defects in CFRP materials using ultrasonic signal processing." *Ultrasonics*, 48, **2008**: 731 - 738.
- Berens A.R., Hopfenberg H.B.,. "Diffusion and relaxation in glass polymer powders:2. Separation of diffusion and relaxation parameters." *Polymers*, 19(5), **1978**: 489-496.
- Blanco I, Cicala G, Costa M, Recca A. " Development of an epoxy system characterized by low water absorption and high thermomechanical performances. ." *Journal of Applied Polymer Science* 100(6):, **2006**: 4880–4887.
- Bortolin A., Aouda F.A., Longo E., Mattoso L.H.C. "Investigation of water absorption process in polysaccharide hydrogels: effect of ionic charge, presence of salt, monomer and polysaccharide Concentrations." *Polymers*, 22(4), **2012**: 311-317.
- Botelho E.C., Pardini L. C., Rezende M. C. "Hygrothermal effects on the shear properties of carbon fibre/epoxy composites." *Journals of Material Science*, Vol. 41, Issue 21, **2006**: 7111-7118.
- Breuer O., Sundararaj U. "Big Returns from Small Fibers: A Review of Polymer/Carbon Nanotubes Composites." *Polymer Composites*, December 2004, Vol.25, No.6, **2004**: 630-645.
- Brill R.P., Palmese G.R.,. "Cure behavior of DGEBA vinyl ester–styrene resins near silane-treated interfaces." *Journal of applied polymer science*, 101(5), **2006**: 2784-2792.
- Brondsted P., Lilholt H., Lystrup A. "Composite materials for wind power turbine blades." *Ann Rev Mater Res*, 35, **2005**: 505 - 538.
- Brun E., Rain P., Teissedre G., Guillermin C., Rowe S. "Hygrothermal aging of a filled epoxy resin." *2007 International Conference on Solid Dielectrics*. Winchester, UK: Schneider Electric, **2007**. 3.
- Bryning M.B., Islam M.F., Kikkawa J.M., Yodh A.G. "Very low conductivity threshold in bulk isotropic single-walled carbon nanotube-epoxy composites." *Adv. Matter*, 17, **2005**: 1186 - 1191.
- Burkholder G.L., Kwon Y.W., Pollak R.D. "Effect of carbon nanotube reinforcement on fracture strength of composite adhesive joints." *Journal of Materials Science*, 46(10), **2011**: 3370-3377.
- Callister W.D. *Fundamentals of Material Science and Engineering*. New York: John Wiley & Sons, p. S-162, **2001**.
- Calventus Y., Montserrat S., Hutchinson JM. "Enthalpy relaxation of non-stoichiometric epoxy-amine resins." *Polymer*, 42, **2001**: 7081 - 7093.
- Carter H.G., Kibler K.G. "Langmuir-type model for anomalous moisture diffusion in composite resins." *J. Compos. Mater.*,12, **1978**: 118-31.
- Castangs M., Hosten B. "Lamb and SH waves generated and detected by air-coupled ultrasonic transducers in composite material plates." *NDT&E International*, 34, **2001**: 249 - 258.

- Chaki S., Harizi W., Bourse G., Ourak M. "Multi-technique approach for non destructive diagnostic of structural composite materials using bulk ultrasonic waves, guided waves, acoustic emission and infrared thermography." *Composites Part A*, 78, **2015**: 358-361.
- Chakrabortya G., Gupta K., Meikap A.K., Babu R., Blau W.J. "Synthesis, electrical and magnetotransport properties of polypyrrole - MWCNT nanocomposite." *Solid State Communications*, 152, **2012**: 13-18.
- Chakrapani S.K., Dayal V. "The interaction of Rayleigh waves with delaminations in composite laminates." *J. Acoust. Soc. Am.*, 135(5), **2014**: 2646 - 2653.
- Chakraverty A.P., Mohanty U.K., Ray B.C.,. "Response to sea water immersed GFRP composite to thermal shock." *Journal of Materials and Metallurgical Engineering*, 3(1), **2013**: 34-41.
- Chakraverty A.P., Mohanty U.K., Mishra S.C., Satapathy A.,. "Sea Water ageing of GFRP composites and the dissolved salts." *4th National Conference on Processing and Characterization of Materials. Materials Science and Engineering*, 75, **2015**. 15.
- Chandrasekaran V.C.S., Santare M.H., Krishnan P., Advani S.G. "Amino functionalization of MWCNTs and their effect on ILSS of hybrid nanocomposites." *Compos Interface*, 18(4), **2011**: 339 - 355.
- Chateauminois A., Chabert B., Soulier J.P. and Vincent L. "Hygrothermal Ageing Effects on the Static Fatigue of Glass/Epoxy Composites." *Composites*, Vol. 24, Issue 7, **1993**: 547-555.
- Chen A.S., Amod D.P., Harris B. "In situ Monitoring in Real Time of Fatigue Damage Growth in Composite Materials by Acoustography." *Composite Science and Technology*, 61, **2001**: 2437 - 2443.
- Chen X., Wang J., Lin M., Zhong W., Feng T., Chen X., Chen J., Xue F.,. "Mechanical and thermal properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes." *Materials science and engineering*, 492(1-2), **2008**: 236-242.
- Chen Z-K., Yang J-P., Ni Q-Q., Fu S-Y., Huang Y-G. "Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties." *Polymer*, 50, **2009**: 4753 - 4759.
- Chifu A.F., Iroh J.O.,. "Short term isothermal aging of epoxy resin-carbon fiber composites." *Polym. Compos.*, 17(3), **1996**: 408-413.
- Chin JW., Nguyen T., Aouadi K.,. "Effects of environmental exposure on fiber-reinforced plastic (FRP) materials used in construction." *J Compos Technol Res.*, 19(4), **1997**: 205 - 213.
- Chou T.W. Microstructural design of fiber composites. Cambridge, UK: Cambridge University Press, **2005**.
- Chow W.S., Chang L.N., Jaafar M.,. "Flame retardant epoxy hybrid composite laminates prepared by vacuum-assisted resin infusion technique." *Journal of Composite Materials*, 49(12), **2015**: 1471-1481.
- Chua T.P., Mariatti M., Azizan A., Azura A.R. "The effect of surface functionalized multiwalled carbon nanotubes on the properties of poly(dimethyl siloxane) nanocomposites." *Composite Science and Technology*, 70(4), **2010**: 671 - 677.
- Ci L., Bai J. "The reinforcement role of carbon nanotubes in epoxy composites with different matrix stiffness." *Compos Sci Technol*, 66, **2006**: 599 - 603.

Cividanes L.S., Simonetti E.A.N., Moraes M.B., Fernandes F.W., Thim G.P. "Influence of carbon nanotubes on epoxy resin cure reaction using different techniques: A comprehensive review." *Polymer Engineering and Science*, 54(11), **2014**: 2461-2469.

Clark H.A., Plueddemann E.P., "Bonding of silane coupling agents in glass reinforced plastics. ." *Mod Plast*, 40 , **1963**: 133–5, 137–8, 195–6.

Cotugno S, Mensitieri G, Musto P, Sanguigno L. "Molecular interactions in and transport properties of densely cross-linked networks: A time-resolved FT-IR spectroscopy investigation of the epoxy/H₂O system." *Macromolecules* 38(3), **2005**: 801-811.

Cunha J.A.P., Costa M. L. , Rezende M.C. "Study of the hygrothermal effects on the compression strength of carbon tape/epoxy composites." *Latin American Journal of Solids and Structures*, 5, **2008**: 157 - 170.

Dalina W.A.D.W, Mariatti M., Ramlee R., Ishak Z.A.M., Mohamed A.R. "Comparison on the properties of Glass Fiber/MWCNT/EPoxy and Carbon Fiber/MWCNT/EPoxy Composites." *Advanced Materials Research*, Vol. 858, **2014**: 32-39.

Datta D., Kishore N.N. "Features of ultrasonic wave propagation to identify defects in composite materials modelled by finite element method." *NDT & E International*, 29 (4), **1996**: 213-223.

Davies P., Mazeas F., Casari P. "Sea Water Aging of Glass Reinforced Composites: Shear Behaviour and Damage Modelling." *Journal of Composite Materials*, 35, **2001**: 1343 - 1372.

Davies P., Evrard G. "Accelerated ageing of polyurethanes for marine applications." *Polymer Degradation Stability*, 92, **2007**: 1455-1464.

De Angelis G., Meo M., Almond D.P., Pickering S.G., Angioni S.L. "A new technique to detect defect size and depth in composite structures using digital shearography and unconstrained optimization ." *NDT & E International*, 45(1), **2012**: 91-96.

De Angelis G., Dati E., Bernabei M., Leccese F. "Development on aerospace composite structures investigation using thermography and shearography in comparison to traditional NDT methods." *Metrology for Aerospace*. IEEE, **2015**.

Demcenko A., Žukauskas E., Kažys R., Voleišis A. "Investigation of interaction of the Lamb wave with delamination type defect in GLARE composite using air-coupled ultrasonic technique." *Forum Acusticum*, **2005**.

Diamanti K., Hodgkinson J.M., Soutis C. "Damage detection of composite laminates using PZT generated Lamb waves, in: D. Balageas (Ed.)." *Proceedings of the First European Workshop on Structural Health Monitoring*. Paris, France, July **2002**: 398 - 405.

Diez-Pascual A., Ashrafi B., Naffakh M., Gonza lez-Dominguez J., Johnston A., Simard B., Martinez M., Gomez-Fatou M. " Influence of carbon nanotubes on the thermal, electrical, and mechanical properties of poly(ether ether ketone)/glass fiber laminates." *Carbon*, **2011**: 49.

Ellyin F., Rohrbacher C. "Effect of aqueous environment and temperature on glass-fiber epoxy resin composites." *J. Reinf. Plast. Compos.*, 19(17), **2000**.

- Fan Z., Santare M.H., Advani S.G. "Interlaminar shear strength of glass fiber reinforced epoxy composites enhanced with multi-walled carbon nanotubes." *Composites: Part A*, 39, **2008**: 540-554.
- Farbod M., Mobini N., "Physical properties, thermal stability, and glass transition temperature of multi-walled carbon nanotube/polypyrrole nanocomposites." *Composite Interfaces*, 21(8), **2014**: 737-747.
- Favis B.D., Blanchard L.P., Leonard J., Prud'Homme R.E., "The interaction of a cationic silane coupling agent with mica. ." *J Appl Polym Sci*, 28:, **2003**: 1235-44.
- Fernandez-Nogroa F., Valea A., Llano-Ponte R., Mondragon I. "Dynamic and mechanical properties of DGEBA/poly(propylene oxide) amine based epoxy resins as a function of stoichiometry." *Eur Polym J*, 32, **1996**: 257 - 66.
- Fiedler B., Gojny F.H., Wichmann M.H.G., Nolte M.C.M., Schulte K. "Fundamental aspects of nano-reinforced composites." *Composites Science and Technology*, 66, Vol. 16, **2006**: 3115-3125.
- Fiorea V., Bellab G.Di , Valenza A. "The effect of alkaline treatment on mechanical properties of kenaf fibers and their epoxy composite." *Composites: Part B*, 68, **2015**: 14-21.
- Frisch H.L. "Diffusion in polymers. In: Crank J and Park J (eds.)." 452. London, New York: Academic Press, **1968**.
- Gao L., Chou T-W., Thostenson E.T., Godara A., Zhang Z., Mezzo L., "Highly conductive polymer composites based on controlled agglomeration of carbon nanotubes." *Carbon*, 48(9), **2010**: 2649-2651.
- Gao L., Chou T-W., Thostenson E.T., Zhang Z., Coulaud M., "In-situ sensing of impact damage in epoxy/glass fiber composites using percolation carbon nanotube networks." *Carbon*, 49(10), **2011**: 3382-3385.
- Garg P., Singh B.P., Kumar G., Gupta T., Pandey I., Seth R.K., Tandon R.P., Mathur R.B., "Effect of dispersion conditions on the mechanical properties of multi-walled carbon nanotubes based epoxy resin composites." *J Polym Res*, 18, **2011**: 1397 - 1407.
- Garg M., Sharma S., Mehta R. "Pristine and amino functionalized nanotubes reinforced glass fiber epoxy composites." *Composites Part A*, 76, **2015**: 92-101.
- Garg M., Sharma S., Mehta R. Processing of functionalized and pristine carbon nanotube epoxy composites with silane treated glass fiber. *Materials and Manufacturing Processes*, **2016**, DOI: 10.1080/10426914.2016.1176186.
- Gellert E.P., Turkey D.M., "Seawater immersion ageing of glass-fibre reinforced polymer laminates for marine applications." *Composites: Part A*, 30, **1999**: 1259.
- Gelset Inc. "Silane coupling agents." *Applying Silanes*. 2006. www.gelset.co (accessed July 7, **2014**).
- Genedy M., Daghash S., Soliman E., Taha M.M.R. "Improving fatigue performance of GFRP composites using carbon nanotubes." *Fibers*, 3, **2015**: 13-29.
- Geng Y., Liu M.Y., Li J., Shi X.M., Kim J-K. "Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites." *Composites: Part A*, 39, **2008**: 1876 - 1883.
- Ghosh T., Kundu T., Karpur P. "Efficient use of lamb modes for detecting defects in large plates." *Ultrasonics*, 36, **1998**: 791 - 801.

- Godara A., Mezzo L., Luizi F., Warrier A., Lomov S.V., Vuure A.W. van, Gorbatiikh L. , Moldenaers P., Verpoest I. "Influence of carbon nanotube reinforcement on the processing and the mechanical behaviour of carbon fiber/epoxy composites." *Carbon*, 47, **2009**: 2914-2923.
- Gojny F.H., Nastalczyk J., Roslaniec Z., Schulte K., "Surface modified carbon nanotubes in CNT/epoxy-composites." *Chem Phys Lett.* 370,, **2003**: 820 - 824.
- Gojny F.H., Schulte K. "Functionalisation effect on the thermo-mechanical behavior of multi-wall carbon nanotube/epoxy composites." *Compos Sci Technol*, 64, **2004a**: 2303 - 2308.
- Gojny F.H., Wichmann M.H.G. , K€opke U. , Fiedler B. , Schulte K. "Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content." *Journal of Composites Science and Technology* 64, **2004b**: 2363–2371.
- Gojny F.H., Wichmann M.H.G. , Fiedler B. , Bauhofer W., Schulte K. "Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites." *Composites Part A*, 36, **2005a**: 1525-1535.
- Gojny F.H., Wichmann M.H.G. , Fiedler B. , Schulte K. "Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites - A comparative study." *Composites Science and Technology*, 65, **2005b**: 2300 - 2313.
- Gorbatiikh L., Lomov S.V., Verpoest I. "Nano-engineered composites: a multiscale approach for adding toughness to fibre reinforced composites." *Procedia Engineering*, 10, **2011**: 3252-3258.
- Goyal S.L., Sharma S., Jain D., Kishore N.N., "Study of structural, electrical and thermal properties of polyaniline/ZnO composites synthesized by in- situ polymerization." *INDIAN JOURNAL OF PURE AND APPLIED PHYSICS*, 53(7), **2015**: 456-463.
- Grimmer C.S., Dharan C. K. H. "High-cycle fatigue of hybrid carbon nanotube/glass fiber/polymer composites." *Journal of Material Science*, 43, **2008**: 4487-4492.
- Gude M.R., Prolongo S.G., Urena A. "Effect of the epoxy/amine stoichiometry on the properties of carbon nanotube.epoxy composites." *J Therm Anal Calorim*, 108, **2012**: 717 - 723.
- Harb M.S., Yuan F.G. "Non-contact ultrasonic technique for Lamb wave characterization in composite plates." *Ultrasonics*, 64, **2016**: 162-169.
- Harris P.F. *Carbon nanotubes and related structures: New materials for the twenty-first century*. Cambridge: University Press: Cambridge, **1999**.
- Hay T.R., Rose J.L. "Guided wave testing optimization." *Materials Evaluation*, 60 (10), **2002**: 1239 - 1344.
- Hay T.R., Wei L., Rose J.L. "Rapid Inspection of composite skin-honeycomb core structures with ultrasonic guided waves." *Journal of Composite Materials*, Vol. 37, No. 10, **2003**: 929-939.
- Hayashi T., Kawashima K. "Multiple reflections of Lamb waves at a delamination." *Ultrasonics*, 40, **2002**: 193 - 197.
- Hayashi T., Rose J.L. "Guided wave simulation and visualization by a semi-analytical finite element method." *Materials Evaluation*, 61 (1), **2003**: 75 - 79.

Hayashi T., Rose J.L., Kawashima K., Sun Z. "Analysis of Flexural Mode Focusing by a Semi-Analytical Finite Element Method." *J. Acoust. Soc.Am.* **2002**.

He C., Van Velsor J.K., Lee C.M., Rose J.L. "Health monitoring of rock bolts using ultrasonic guided waves." *Quantitative Non Destructive Evaluation*. AIP Proceedings, 820, **2006**: 195 - 201.

Hernandez-Pérez A., Avile's a A., Pat A.M , Valadez-González A., Herrera-Franco P.J. , Bartolo-Pérez P. "Effective properties of multiwalled carbon nanotube/epoxy composites using two different tubes." *Composites Science and Technology*, 68(6), **2008**: 1422–1431.

Hirai Y., Hamada H., Kim J-K. "Impact response of woven glass fabric composites - I. Effect of Fiber Surface Treatment." *Composites Science and Technology*, 58, **1998**: 91 - 104.

Hong K.M., Kang Y.J., Choi I.Y., Kim S.J., Lee G.D. "Ultrasonic signal analysis according to laser ultrasound generation position for the detection of delamination in composites ." *Journal of Mechanical Science and Technology*, 29(12), **2015**: 5217-5222.

Hossain M.K., Chowdhury Md M.R., Salam M.B., Malone J., Hosur M.V., Jeelani S., Bolden N.W. "Improved thermomechanical properties of carbon fiber reinforced epoxy composites using Amino Functionalized XDCNT." *Journal of Applied Polymer Science*, **2014**: 40709-40721.

Hosur M.V., Rahman T., Brundidge-Young S., Jeelani S. "Mechanical and Thermal Properties of Amine Functionalized Multi-walled Carbon Nanotubes Epoxy-Based Nanocomposite." *Composite Interfaces* , 17(2-3), **2010**: 197-215.

Huang Y.Y., Ahir S.V., Terentjev E.M. "Dispersion rheology of carbon nanotubes in a polymer matrix." *Phys Rev B*, 73, **2006**: 125422-1-9.

Hung Y.Y., Luo W.D., Lin L., Shang H.M. "Evaluating the Soundness of Bonding Using Shearography." *Composite Structures*, 50, **2000**: 353 - 362.

Iglesias J.G., Benito J.G., Aznar A.J., Bravo J., Baselga J. "Effect of Glass Fiber surface treatments on mechanical strength of epoxy based composite materials." *Journal of Colloid and Interface Science*, 250, **2002**: 251 - 260.

Iijima S., I. "Helical microtubules of graphitic carbon." *Nature*, 354 , **1991**: 56-58.

Isa M.T., Usman S., Ameh A.O., Ajayi O.A., Omorogbe O., Ameuru S. U. "The Effect of Fiber Treatment on the Mechanical and Water Absorption Properties of Short Okra/Glass Fibers Hybridized Epoxy Composites." *International Journal of Materials Engineering*, 4(5), **2014**: 180-184.

Iwahori Y., Ishiwata S., Sumizawa T., Ishikawa T. "Mechanical properties improvements in two-phase and three-phase composites using carbon nanofiber dispersed resin." *Compos Part A: Appl Sci*, 36 (10), **2005**: 1430 - 1439.

Jang J., Bae J., Lee K.,. "Synthesis and characterization of polyaniline nanorods as curing agents and nanofillers for epoxy matrix composites." *Polymer*, 46(11), **2005**: 3677-3684.

Jiang X., Kolstein H., Bijlaard F.S.K. "Moisture diffusion and hygrothermal aging in pultruded fibre reinforced polymer composites of bridge decks." *Materials and Design*, 37, **2012**: 304-312.

- Jiang X., Kolstein H., Bijlaard F.S.K., "Effects of hygrothermal aging on glass-fibre reinforced polymer laminates and adhesive of FRP composite bridge: Moisture diffusion characteristics." *Compos Part A: Appl. Sci. Manuf.* (57), **2013**: 49–58.
- Jin Z., Khunlavit C., Shuai H., Chun H., Wang. "Hybrid composite laminates reinforced with glass/carbon woven fabrics for lightweight load bearing structures." *Materials and Design*, 36, **2011**: 75 - 80.
- José Humberto S. Almeida Jr., Souza S.D.B., Botelho E.C., Amico S.C. "Carbon fiber-reinforced epoxy filament-wound composite laminates exposed to hygrothermal conditioning." *Journal of Materials Science*, 51(9), **2016**: 4697-4708.
- Kar K.K., Sharma S.D., Mohanty A., Kumar P., "Short-term Effect of Distilled Water, Seawater and Temperature on the Crushed and Interlaminar Shear Strength of Fiber Reinforced Plastic Composites made by the newly proposed rubber pressure molding technique." *Polymer Composites*, **2008**: 670-691.
- Karbhari V.M., Zhang S., "E-glass/vinylester composites in aqueous environments-I: Experimental Results." *Applied Composite Materials*, 10, **2003**: 19 - 48.
- Kessler S.S., Spearing S.M., Scoutis C. "Damage detection in composite materials using Lamb Wave methods." *Smart Materials and Structures*, 11, **2002**: 269 - 278.
- Kim J.K., Mai Y-W. "High strength, high fracture toughness fibre composites with interface control - a review." *Compos Sci Technol*, 41(4), **1991**: 333 - 378.
- Kim J.K., Mai Y.W. "Interfaces in composites, In: Chou TW, editor." *Materials science and technology: structure and properties of composites*, 13, **1993**: 229 - 289.
- Kim J-K., Sham M-L., Jingshen W. "Nanoscale characterization of interphase in silane treated glass fiber composites." *Composites: Part A*, 32, **2001**: 607 - 618.
- Kim M., Park Y.B., Okoli O.I., Zhang C. "Processing, characterization, and modeling of carbon nanotube-reinforced multiscale composites." *Composites Science and Technology*, 69(3-4), **2009**: 335-342.
- Kim M.T., Rhee K.Y., Lee J.H., Hui D., Lau A.K.T. "Property enhancement of a carbon fiber/epoxy composite by using carbon nanotubes." *Composites: Part B*, 42, **2011**: 1257-1261.
- Kim Young-Han, Kim Dae-Hyun, Han Jung-Ho, Kim Chun-Gon. "Damage assessment in layered composites using spectral analysis and Lamb Wave." *Composites: Part B*, 38, **2007**: 800 - 809.
- Kinloch I.A., Roberts S.A., Windle A.H. "A rheological study of concentrated aqueous nanotube dispersions." *Polymer*, 43, **2002**: 7483 - 7491.
- Kishore N. N., Sridhar I., Iyengar N.G.R. "Finite element modelling of the scattering of ultrasonic waves by isolated flaws." *NDT & E International*, 33(5), **2000**: 297-305.
- Kootsookos A., Mouritz A.P. "Seawater durability of glass- and carbon-polymer composites." *Composites Science and Technology*, 64, **2004**: 1503-1511.
- Kovacs J.Z., Andresen K., Pauls J.R., Garcia C.P., Schossig M., Schulte K. "Analyzing the quality of carbon nanotube dispersions in polymers using scanning electron microscopy." *Carbon*, 45, **2007**: 1279 - 1288.

- Krawczak P., Pabiot J. "Influence of the loading mode and the hydrothermal environment on the contribution of the interface to the cohesion of glass/epoxy composites." *Polym. Compos.*, 3(4), **1995**: 299-306.
- Ku-Herrera J.J., Aviles F., Nistal A., Cauich-Rodríguez J.V., Rubio F., Rubio J., Bartolo-Pérez P. "Interactions between the glass fiber coating and oxidized carbon nanotubes." *Applied Surface Science*, 330, **2015**: 383-392.
- Kundu T. Potel C., Belleval J.F. "Importance of Near lamb mode imaging in multilayered composite plates." *Ultrasonics*, 39, **2001**: 283-290.
- Lagrange A., Melennec C., Jacquernet R., "Influence of various stress conditions on the moisture diffusion of composites in distilled water and natural sea water." *Durability of Polymer Based Composites Systems for Structural Applications*, **1991**: 385.
- Laoubi K., Belloul N., Benyahia A.A., Serier A., Ouali N. "Effects of Ageing in Marine Environment on Glass Fibre/Unsaturated Polyester Composite." *Applied Mechanics and Materials*, Vol. 146, **2012**: 51-63.
- Lata D. "Fabrication of Decorative Fluorescent Composite Material." *Department of Physics, National Institute of Technology Rourkela*, **2000**: 6-7.
- Lee H., Neville K. "Spravochnoe rukovodstvo po epoksidnim smolam." *Moskva-Leningrad: Energija*, **1973**: 320.
- Li C., Chou T-W. "Electrical conductivities of composites with aligned carbon nanotubes." *J Nanosci Nanotechnol*, 9(4), **2009**: 2518 - 2524.
- Li J., Ma P.C., Chow W.S., To C.K., Tang B.Z., Kim J.K. "Correlations between percolation threshold, dispersion state and aspect ratio of carbon nanotube." *Adv Funct Matter*, 17, **2007**: 3207 - 3215.
- Li M., Boggs M., Beebe T.P., Huang C.P. "Oxidation of single-walled carbon nanotubes in dilute aqueous solutions by ozone as affected by ultrasound." *Carbon*, **2008**, 46(3): 466-475.
- Lijie C., JinBo B. "The reinforcement role of carbon nanotubes in epoxy composites with different matrix stiffness." *Composites Science and Technology*, 66, **2006**: 599-603.
- Liu L., Avioli M.J., Rose J.L. "Incident angle selection for the guided wave inspection of pipe defects." *Insight*, 43(2), **2001**: 33 - 38.
- Liu Lu-Qi, Wagner H.D. "A comparison of the mechanical strength and stiffness of MWNT-PMMA and MWNT-epoxy nanocomposites." *Composite Interfaces*, 14(4), **2007**: 285-297.
- Liu X., Zhou C., Jiang Z. "Damage localization in plate-like structure using built-in PZT sensor network." *Smart Structures and Systems*, 9(1), **2012**.
- Liu Z.H., Yu H.T., He C.F., Wu B. "Delamination damage detection of laminated composite beams using air coupled ultrasonic transducers ." *Sci. China Phys. Mech. Astron.*, 56 (7) , **2013**: 1269-1279.
- Lopez J., Rico M., Montero B., Diez J., Ramirez C. "Polymer blends based on an epoxy-amine thermoset and a thermoplastic." *J. Therm Anal Calorim.*, Vol. 95, **2009**: 369-376.
- Luo Y., Zhao Y., Cai J., Duan Y., Du S. "Effect of amino-functionalization on the interfacial adhesion of multi-walled carbon nanotubes/epoxy nanocomposites." *Materials and Design*, 33, **2012**: 405-412.

- Ma P.C., Kim J-K., Tang B.Z. "Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites." *Composites Science and Technology*, 67, **2007**: 2965 - 2972.
- Ma P.C., Kim J-K., Tang B.Z. "Functionalization of carbon nanotubes using a silane coupling agent." *Carbon*, 44, **2006**: 3232-8.
- Ma P.C., Siddiquia N.A., Maromb G., Kima J.K. "Dispersion and Functionalization of Carbon Nanotubes for Polymer-Based Nanocomposites: A Review." *Composites Part A- Appl. Science and Manufacturing*. 41, no. 10, **2010**: 1345-1367.
- Mahjouba R., Yatimb J.M., Samb A.R.M., Hashemi S.H. "Tensile properties of kenaf fiber due to various conditions of chemical fiber surface modifications." *Construction and Building Materials*, 55, **2014**: 103-113.
- Mallick P.K. *Fibre reinforced polymers by*. New York: CRC Press, **2007**.
- Martone A., Formicola C., Giordano M., Zarrelli M. "Reinforcement efficiency of multi-walled carbon nanotube/epoxy nano composites." *Composites Science and Technology*, Volume 70, Issue 7, **2010**: 1154–1160.
- Mawhinney DB., Naumenko V., Kuznetsova A., Yates JT., Liu J., Smalley RE. "Infrared spectral evidence for the etching of carbon nanotubes: ozone oxidation at 298 K." *J. Am. Chem. Soc.*, 122, **2000**: 2383-4.
- May CA. "Epoxy resins: chemistry and technology, 2nd ed." 907-9. New York: Marcel Dekker Inc., **1988**.
- Mehta G., Drzal L.T., Mohanty A.K., Misra M. "Effect of fiber surface treatment on the properties of biocomposites from nonwoven industrial hemp fiber mats and unsaturated polyester resin." *Journal Of Applied Polymer Science*, 99(3), **2006**: 1055-1068.
- Meyer F., Sanz G., Eceiza A., Mondragon I., Mijovie J. "The effect of stoichiometrix and thermal history during cure on structure and properties of epoxy networks." *Polymer*, 36, **1995**: 1407 - 1414.
- Milowska K., Birowska M., Majewski J.A. "Mechanical and electrical properties of carbon nanotubes and graphene layers functionalized with amines." *Diamond and Related Materials*, 23, **2012**, 167 - 171.
- Min-Feng Yu, Lourie O., Dyer M.J., Moloni K., Kelly T.F., Ruoff R.S. "Strength and Breaking Mechanism Of Multiwalled Carbon Nanotubes Under Tensile Load." *Science*, 28(287), **2000**: 637-640.
- Moll J., Torres-Arredondo M.A., Fritzen Claus-Peter. "Computational aspects of guided wave based damage localization algorithms in flat anisotropic structures." *Smart Structures and Systems*, 10(3), **2012**.
- Montazeri A., Chitsazzadeh M., "Effect of sonication parameters on the mechanical properties of multi-walled carbon nanotube/epoxy composites." *Materials and Design*, 56, **2014**: 500-508.
- Monthieux M., Smith BW., Burtiaux B., Claye A., Fischer JE., Luzzi DE. "Sensitivity of single-wall carbon nanotubes to chemical processing: an electron microscopy investigation." *Carbon*, 39, **2001**: 1251 - 72.
- Morales J., Olayo MG, Cruz GJ, Herrera-Franco P , Olayo R. "Plasma modification of cellulose fibers for composite materials." *Journal of applied polymer science* 101 (6), **2006**: 3821-3828.

- Morgan RJ, Kong FM, Walkup CN. "Structure-property relations of polyethertriamine-cured bisphenol-A-diglycidyl ether epoxies." *Polymer*, 25, **1984**: 375 - 86.
- Mourad A-H. I., Magid B. M. A-M., Maaddawy T. E-L., Grami M.E. "Effect of seawater and warm environment on glass/epoxy and glass/polyurethane composites." *Appl Compos Mater*, 17, **2010**: 557 - 573.
- Mula S., Bera T., Ray P.K., Ray B.C.,. "Effect of Hydrothermal ageing on mechanical behaviour of sub-zero weathered GFRP composites." *J. Reinforced Plastics and Composites*, 25(6), **2006**: 673-680.
- Muthirakkal S., Murthy H.N.R.N., Krishna M., Rai K.S., Karippal J.J.,. "Hygrothermic behavior of carbon/vinylester, glass/vinylester, carbon/epoxy and glass/epoxy composites." *Iranian Polymer Journal*, 19(2), **2010**: 89-103.
- Na W.B., Kundu T. "Underwater pipeline inspection using guided waves." *J. Pressure Vessel Technol.* 124, **2002**: 196 - 200.
- Najafi E., Kim J-Y, Han S-H, Shin K. "UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion." *Colloids and SurfacesA: Physicochemical and Engineering Aspects*, **2006**, 284-285: 373-378.
- Nattapat M., Marimuthu S., Kamara A. M., Nekouie Esfahani M. R. "Laser Surface Modification of Carbon Fiber Reinforced Composites." *Materials and Manufacturing Processes*, 30(12), **2015**: 1450-1456.
- Netravali A.N., Fornes R.E., Gilbert R.D., Memory J.D.,. "Effects of water sorption at different temperatures on permanent changes in an epoxy." *Journal of Applied Polymer Science*, 30, **1985**: 1573-1578.
- Nogueira P., Ramirex C., Torres A., Abad M.J., Cano J., Lopez J. et al.,. "Effect of water sorption on the structure and mechanical properties of an epoxy resin system." *J. Appl. Polym. Sci.*, 80, **2001**: 71 - 80.
- Noobut W., Koeing J.L. "Interfacial behavior of Epoxy/E-Glass fiber composites under wet-dry cycles by Fourier Transform Infrared Microspectroscopy." *Polymer Composites*, Vol. 20, No. 1, **1999**: 38-47.
- Okafor A.C., Otieno A.W., Dutta A., Rao V.S. "Detection and Characterization of High-Velocity Impact Damage in Advanced Composite Plates Using Multi-Sensing Techniques." *Composite Structures*, 54, **2001**: 289 - 297.
- Palmese GR., McCullough RL. "Effect of epoxy-amine stoichiometry on cured resin material properties." *J Appl Polym Sci.*, 46, **1992**: 1863 - 73.
- Palumbo D., Tamborrino R., Galietti U., Aversa P., Tatì A., Luprano V.A.M. "Ultrasonic analysis and lock-in thermography for debonding evaluation of composite adhesive joints." *NDT&E International*, 78, **2016**: 1-9 .
- Pantano C.G., Wittberg T.N. "XPS analysis of silane coupling agents and silane-treated E-glass fibers." *Surface and Interface Analysis*, Vol. 15, **1990**: 498 - 501.
- Parida C., Dash S.K., Das S.C. "Effect of Fiber Treatment and Fiber Loading on Mechanical Properties of Luffa-Resorcinol Composites." *Indian Journal of Materials Science*, **2015**: 6.

Park S., Jin J., Lee J. "Influence of silane coupling agents on the surface energetics of glass fibers and mechanical interfacial properties of glass fiber-reinforced composites." *Journal of Adhesion Science and Technology*, 14(13), **2000**: 1677-1689.

Park C., Ounaies Z., Watson K.A., Crooks R.E., Smith J., Lowther S.E., Connell J.W., Siochi E.J., Harrison J.S., Clair T.L.S. "Dispersion of single wall carbon nanotubes by in situ polymerization under sonication." *Chemical Physics Letters*, 364, **2002**: 303 - 308.

Park S.J., Jin J.S. "Effect of silane coupling agent on mechanical interfacial properties of glass fiber-reinforced unsaturated polyester composites." *J.Polym.Sci.Polym.Phys.*, 41(1), **2003**: 55.

Park S.J., Joeng H.J., Nah C. "A study of oxofluorination of multi-walled carbon nanotubes on mechanical interfacial properties of epoxy matrix nanocomposites." *Mater Sci Eng A*, 385, **2004**: 13 - 6.

Paszkiwicz S., Pilawka R., Zenker M., Czulak A., Rosłaniec Z. "Detailed study on interfacial interactions in epoxy composites cured with 1-buthylimidazole containing functionalized carbon nanotubes." *Composite Interfaces*, 22(7), **2015**: 629-649.

Pavlakovic B.N., Lowe M.J.S., Cawley P. "High frequency low loss ultrasonic modes in imbedded bars." *International Journal of Applied Mechanics*, 68, **2001**: 67 - 75.

Pe´rez-Pacheco E., Cauich-Cupul J. I., Valadez-González A., Herrera-Franco P. J. "Effect of moisture absorption on the mechanical behavior of carbon fiber/epoxy composites." *J Mater Sci*, 48, **2013**: 1873-1882.

Pereira A.A.C., Almeida J.R.M. "Effect of the hardener to epoxy monomer ratio on the water absorption behavior of the DGEBA/TETA epoxy system." *Polimeros*, **2016**: <http://dx.doi.org/10.1590/0104-1428.2106>.

Pistone E., Li K., Rizzo P. "Noncontact monitoring of immersed plates by means of laser induced ultrasounds ." *Structural Health Monitoring*, 12(5-6) , **2013**: 549-565.

Pistone E., Rizzo P. "On the use of an array of ultrasonic immersion transducers for the nondestructive testing of immersed plates." *Nondestructive Testing and Evaluation*, 30(1), **2015**: 26-38.

Popineau S., Rondeau-Mouro C., Sulpice-Gaillet C., Shanahan MER. "Free/bound water absorption in an epoxy adhesive." *Polymer*, 46, **2005**: 10733-40.

Prasad M.S., Balasubramaniam K., Krishnamurthy C.V. "Structural health monitoring of composite structures using Lamb wave tomography." *Smart materials and structures*, 13(5), **2004**.

Pritchard G., Speake S.D. "The use of water absorption kinetic data to predict laminate property changes." *Composites*, 18(3), **1987**: 227-232.

Prolongo S.G., Gude M.R., Urena A. "The curing process of epoxy/amino-functionalized MWCNTs: Calorimetry, Molecular Modelling, and Electron Microscopy." *Journal of Nanotechnology*, **2010**: 11.

Prolongo S.G., Gude M.R., Ureña A. "Water uptake of epoxy composites reinforced with carbon nanofillers." *Composites: Part A*, 43, **2012**: 2169 - 2175.

- Providakis C.P., Triantafillou T.C., Karabalis D., Papanicolaou A., Stefanaki K., Tsantilis A., Tzoura E. "Simulation of PZT monitoring of reinforced concrete beams retrofitted with CFRP." *Smart Structures and Systems*, 14(5), **2014**.
- Punnamurthy R., Sampathkumar D., Bennehalli B., Patel R., Venkateshappa S.C. "Abaca Fiber Reinforced Epoxy Composites: Evaluation of Impact Strength." *International Journal of Sciences: Basic and Applied Research*, 18(2), **2014**: 305-317 .
- Putkis O., Dalton R.P., Croxford A.J. "The anisotropic propagation of ultrasonic guided waves in composite materials and implications for practical applications ." *Ultrasonics*, 65, **2016**: 390-399.
- Qian H., Bismarck A., Greenhalgh E.S., Kalinka G., Shaffer MSP., "Hierarchical composites reinforced with carbon nanotube grafted fibers: the potential assessed at the single fiber level." *Chemistry of Materials*, 20(5), , **2008**: 1862-1869.
- Qian H., Bismarck A., Greenhalgh E.S., Kalinka G., Shaffer MSP. "Carbon nanotube grafted carbon fibres: a study of wetting and fibre fragmentation." *Composites Part A: Applied science and manufacturing*, 41 (9), **2010a**: 1107-1114.
- Qian H., Bismarck A., Greenhalgh E.S., Kalinka G., Shaffer MSP., "Synthesis and characterisation of carbon nanotubes grown on silica fibres by injection CVD." *Carbon*, 48(1), **2010b**: 277-286.
- Quaresimin M., Varley R.J. "Understanding the effect of nano-modifier addition upon the properties of fiber reinforced laminates." *Compos Sci Technol*, 68 (3-4), **2008**: 718 - 726.
- Raghavendra M., Manjunatha C.M., Peter M.J., Venugopal C.V., Rangavittal H.K. "Effect of moisture on the mechanical properties of GFRP composite fabric material." *International Symposium of Research Students on Material Science and Engineering*, **2004**: 7.
- Rahatekar S.S., Koziol K.K.K., Butler S.A., Elliott J.A., Shaffer M.S.P., Mackley M.R. "Optical microstructure and viscosity enhancement for an epoxy resin matrix containing multiwall carbon nanotubes." *J Rheol*, 50(5), **2006**: 599 - 610.
- Rahman M.M., Zainuddin S., Hosur M.V., Malone J.E., Salam M.B.A., Kumar A., Jeelani S. "Improvements in mechanical and thermo-mechanical properties of e-glass/epoxy composites using amino functionalized MWCNTs." *Composite Structures*, 94, **2012**: 2397 - 2406.
- Ramadas C., Balasubramaniam K., Joshi M., Krishnamurthy C.V. "Characterisation of rectangular type delaminations in composite laminates through B-and D-scan images generated using Lamb Waves." *NDT&E International*, 44, **2011a**: 281 - 289.
- Ramadas C., Hood A., Padiyar J., Balasubramaniam K., Joshi M. "Sizing of Delamination Using time-of-flight of the Fundamental Symmetric Lamb Modes." *Journal of Reinforced Plastics and Composites*, 30(10), **2011b**: 856-863.
- Ramana G. V., Padya B., Kumar R. N. ,Prabhakar K. V. P., Jain P.K. "Mechanical properties of multi-walled carbon nanotubes reinforced polymer nanocomposites." *Indian Journal of Engineering and Material Sciences*, **2010**: 331-337.
- Ramirez F.A., Carlsson L. A., Acha B. A. "Evaluation of water degradation of vinylester and epoxy matrix composites by single fiber and composite tests." *Journal of Material Science*, Vol. 43, **2008**: 5230-5242.

- Rao P. S., Husain M.M., Shankar D.V.R. "Hygrothermal characterization of GFRP laminates subjected to different water conditions." *IOSR Journal of Mechanical and Civil Engineering*, Vol. 1, Issue 1, **2012**: 12-25.
- Rao P.S., Husain M.M., Shankar D.V.R. "An Investigation on Strength Degradation of Gfrp laminates under environmental impact." *International Journal of Composite Materials*, Vol. 2, No. 4, **2014**: 48-52.
- Ratnam C., Ben B.S., Ben B.A. "Optimization of Lamb Wave propagation parameters for damage detection in composite materials." *JP Journal of Solids and Structures*, 2, **2008**: 69 - 82.
- Ray B.C. "Effects of thermal and cryogenic conditionings on mechanical behavior of thermally shocked glass fiber-epoxy composites." *Journal of Reinforced Plastics and Composites*, 24(7), **2005**: 713-717.
- Rhee K.Y., Lee S.M., Park S.J. "Effect of hydrostatic pressure on the mechanical behavior of seawater - absorbed carbon/epoxy composite." *Matr. Sci. and Engg. A*, 384, **2004**: 308-313.
- Rico M., Lopez J., Bouza R.,. "Thermal behavior of blends based on a thermoplastic-modified epoxy resin with a crosslinking density variation." *J Therm Anal Calorim.*, Vol. 105, **2011**: 599-606.
- Rizzo P., Han Jian-Gang, Ni Xiang-Lei. "Structural Health Monitoring of Immersed Structures by Means of Guided Ultrasonic Waves." *Journal of Intelligent Material Systems and Structures*, 21(14), **2010**: 1397-1407.
- Rizzo P., Pistone E., Bagheri A. "Guided ultrasonic waves for the NDT of immersed plates." *Emerging Technologies in Non-Destructive Testing VI: Proceedings of the 6th International Conference on Emerging Technologies in Non-Destructive Testing*, **2015**: 153.
- Roy S., Xu X., Park S.J.,. "Anamalous moisture diffusion in viscoelastic polymers: modeling and testing." *Trans ASME J Appl Mech.*, 67, **2000**: 391 - 396.
- Saeb M.R., Bakhshandeh E., Khonakdar H.A., Mäder E., Scheffler C., Heinrich G.,. "Cure Kinetics of Epoxy Nanocomposites Affected by MWCNTs Functionalization: A Review." *The Scientific World Journal*, , **2013**: 14.
- Sager R.J., Klein P.J., Lagoudas D.C., Zhang Q., Liu J., Dai L., Baur J.W. "Effect of carbon nanotubes on the interfacial shear strength of T650 carbon fiber in an epoxy matrix." *Composites Science and Technology*, 69(7-8), **2009**: 898-904.
- Salam M.B.A., Hosur M.V., Zainuddin S., Jeelani S.,. "Improvement in mechanical and thermo-mechanical properties of epoxy composite using two different functionalized multi-walled carbon nanotubes." *Open Journal of Composite Materials*, 3, **2013**: 1-9.
- Salvetat J.P., Bonard J.M., Thomson N.H., Kulik A.J., Forro L., Benoit W., Zuppiroli L. "Mechanical properties of carbon nanotubes." *Applied Physics A: Materials Science and Processing* 69, July **1999**: 255-260.
- Sanchez M., Campo M., Suarez A.J, Urena A. "Effect of the carbon nanotube functionalizaton on flexural properties of multiscale carbon fiber/epoxy composites manufactured by VARIM." *Composites: Part B*, 45, **2013**: 1613 - 1619.

Sandler J., Shaffer M.S.P., Prasse T., Bauhofer W., Schulte K., Windle A.H. "Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties." *Polymer*, 40 (21), **1999**: 5967 - 5971.

Schadler L.S., Giannaris S.C., Ajayana P.M., "Load transfer in carbon nanotube epoxy composites." *Applied Physics Letters*, 73 (26), **1998**: 3842-3844.

Scudder L.P., Hutchins D.A., Guo N. "Laser Generated Guided Waves in Fiber-Reinforced Plates - Theory and Experiment." *IEEE Trans. Ultras. Ferro. Freq. Cont.*, 43 (5), **1996**: 870 - 871.

Segovia F., Salvador MD, Sahuquillo O., "Effects of long-term exposure on E-glass composites material subjected to stress corrosion in a saline medium." *J Comp Mater*, 41, **2007**: 2119 - 2128.

Sever K., Sarikanat M., Seki Y., Tavman I.H. "Concentration effect of glycidoxypolytrimethoxysilane on the mechanical properties of glass fiber-epoxy composites." *Polymer Composites* **2009**, 1251 - 1257.

Seyhan A.T., Gojny F.H., Tanoglu M., Schulte K. "Critical aspects related to processing of carbon nanotube/unsaturated thermoset polyester nanocomposites." *Eur. Polym. J.*, 43, **2007**: 374 - 379.

Sham M.L., Kim J.K. "Surface functionalities of multi-walled carbon nanotubes after UV/ozone treatment and TETA treatments." *Carbon*, **2006**, 44: 768-77.

Sham M.L., Li J., Ma P.C., Kim J.K., "Cleaning and functionalization of polymer surfaces and nanoscale carbon fillers by UV/ozone treatment: a review." *J. Compos. Mater.*, 43, **2009**: 1537 - 64.

Sharma S., Mukherjee A. "Longitudinal guided waves for monitoring chloride corrosion in reinforcing bars in concrete." *Structural Health Monitoring*, 9(6), **2010**: 555 - 567.

Sharma S., Mukherjee A. "Monitoring corrosion in oxide and chloride environments using ultrasonic guided waves." *ASCE Journal of Materials in Civil Engineering*, 23(2), **2011**: 207 - 211.

Sharma S., Mukherjee A. "Damage detection in submerged plates using ultrasonic guided waves." *Sadhana*, 39(5), **2014**: 1009-1034.

Sharma S., and Mukherjee A. "Ultrasonic guided waves for monitoring corrosion in submerged plates." *Struct. Control Health Monit.*, 22(1), **2015a**: 19-35.

Sharma S., Mukherjee A. "A Non-Contact Technique for Damage Monitoring in Submerged Plates Using Guided Waves." *Journals of Testing and Evaluation*, 43(4), **2015b**: 1-16.

Shen K., Xu H., Jiang Y., PietraB T. "The role of carbon nanotube structure in purification and hydrogen adsorption." *Carbon*, 42, **2004**: 2315 - 22.

Shen J., Huang W., Wu L., Hu Y., Ye M. "The reinforcement role of different amino-functionalized multi-walled carbon nanotubes in epoxy nanocomposites." *Composites Science and Technology*, 67, **2007a**: 3041-3050.

Shen J., Huang W., Wu L., Hu Y., Ye M., "Thermo-physical properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes." *Composites: Part A*, 38, **2007b**: 1331-1336.

Shokoohi S., Arefazar A. Khosrokhavar R. "Silane coupling agents in polymer based reinforced composites: A review." *Journal of reinforced plastics and composites*, 27(5), **2008**: 473.

Shokrieh M.M., Saeedi A., Chitsazzadeh M., "Evaluating the effects of multi-walled carbon nanotube on the mechanical properties of chopped strand mat/ polyester composites." *Materials and Design*, 56, **2014**: 274-279.

Sihn S., Kim R.Y., Kawabe K., Tsai S.W. "Experimental studies of thin-ply laminated composites." *Composites Science and Technology*, 67(6), **2007**: 996 - 1008.

Siriruk A., Penumadu D., Weitsman Y.J. "Effect of sea environment on interfacial delamination behavior of polymeric sandwich structures." *Composites Science and Technology*, 69, **2009**: 821-828.

Song Y.S., Yuon J.R. "Influence of the dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites." *Carbon*, 43, **2005**: 1378 - 1385.

Starkova O., Buschhorn S.T., Mannov E., Schulte K., Aniskevich A. "Water transport in epoxy/MWCNT composites." *European Polymer Journal*, 49, **2013**: 2138-2148.

Šturm R., Grimberg R., Savin A., Grum J. "Destructive and nondestructive evaluations of the effect of moisture absorption on the mechanical properties of polyester-based composites." *Composites: Part B*, 71, **2015**: 10-16.

Surathi P., Karbhari V.M., *Hygrothermal effects on durability and moisture kinetics of Fiber-reinforced polymer composites*. California: Interim Report, California Department of Transportation, **2006**.

Tang L-C, Zhang H., Han J-H, Wu X-P, Zhang Z. "Fracture mechanisms of epoxy filled with ozone functionalized multi-wall carbon nanotubes." *Composites Science and Technology*, **2011**, 72: 7-13.

Tham W.L., Chow W.S., Ishak Z.A. M. "Simulated body fluid and water absorption effects on poly(methyl methacrylate)/hydroxyapatite denture base composites." *eXPRESS Polymers Letter*, Vol. 4, No. 9, **2010**: 517-528.

Thermo Scientific. "3-Aminopropyltriethoxysilane." *Instructions for applying*. 2012. <http://www.piercenet.com/product/3-aminopropyltriethoxysilane-apt>s (accessed June 18, **2014**).

Thostenson E.T., Chou T.W. "Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites." *Carbon*, 44(14), **2006**: 3022-3029.

Thostenson E.T., Ziaee S., Chou T.W. "Processing and electrical properties of carbon nanotube/vinyl ester nanocomposites." *Compos Sci. Technol.*, 69(6), **2009**: 801 - 804.

Titus E., Ali N., Cabral G., Gracio J., Babu P.R., Jackson M.J., "Chemically functionalized carbon nanotubes and their characterization using thermogravimetric analysis, fourier transform infrared, and raman spectroscopy." *Journal of Materials Engineering and Performance*, 15(2), **2006**: 182-186.

Toyama N., Noda J., Okabe T. "Quantitative damage detection in cross-ply laminates using Lamb wave method." *Composites Science and Technology*, 63, **2003**: 1473 - 1479.

Tsenoglou C.J., Pavlidou S., Papaspyrides C.D., "Evaluation of interfacial relaxation due to water absorption in fiber-reinforced polymer composites." *Compos Sci Technol.*, 66, **2006**: 2855 - 2864.

Tzounis L., Kirstena M., Simona F., Mädera E., Stamm M. "The interphase microstructure and electrical properties of glass fibers covalently and non-covalently bonded with multiwall carbon nanotubes." *Carbon*, 73, **2014**: 310-324.

- Utracki L.A., Kamal M.R. "Clay-Containing Polymer Nanocomposites." *The Arabian Journal for Science and Engineering*, Volume 27, Number 1C, **2002**: 25.
- Valentini L., Armentano I., Puglia D., Kenny J.M. "Dynamics of amine functionalized nanotubes/epoxy composites by dielectric relaxation spectroscopy." *Carbon*, 42(2), **2004**: 323-329.
- Velasco-Santos C., Martinez-Hernandez A.L., Castano V. M. "Carbon nanotube-polymer nanocomposites: The role of interfaces." *Composite Interfaces* , 11(8-9), **2005**: 567-586.
- Wada A., Pak C.H., Kitagawa E., Ito H., Sasaki Y. "Ultrasonic Cure Monitoring of GFRP Laminates." *Advanced Materials Research*, 1110, **2015**: 82-87.
- Wang T.W.H., Blum F.D., Dharani L.R. "Effects of interfacial mobility on flexural strength and fracture toughness of glass/epoxy laminates." *Journal of Materials Science*, 34, **1999**: 4873-4882.
- Wang J.G., Fang Z.P., Gu A.J., Xu L.H., Liu F.,. "Effect of amino-functionalization of multi-walled carbon nanotubes on the dispersion with epoxy resin matrix." *J. Appl. Polym. Sci.*, 100, **2006**: 97 - 104.
- Wang S., Liang Z., Liu T., Wang B., Zhang C. "Effective amino functionalization of carbon nanotubes for epoxy polymer composites." *Nanotechnology*, 17, **2006**: 1551 - 1557.
- Wang Z., Liang Z., Wang B., Zhang C., Kramer L. "Processing and property investigation of single-walled carbon nanotube (SWNT) buckypaper/epoxy resin matrix nanocomposites." *Composites: Part A*, 35, **2004**: 1225 - 1232.
- Wichmann M.H.G., Sumfleth J., Gojny F.H., Quaresimin M., Fiedler B., Schulte K. "Glass-fiber-reinforced composites with enhanced mechanical and electrical properties - Benefits and limitations of a nanoparticle modified matrix." *Engineering Fracture Mechanics*, 73, **2006**: 2346-2359.
- Wilcox P.D., Dalton R.P., Lowe M.J.S., Cawley P. "Mode and transducer selection for long range Lamb wave inspection." *Key Engineering Materials*, 167 - 168, **1999**: 152 -161.
- Wimolkiatisak A.S., Bell J.P.,. "Interfacial shear strength and failure modes of interphase-modified graphite-epoxy composites." *Polymer composites*, 10(3), **2004**: 162-172.
- Wong TC., Broutman L.J.,. "Moisture diffusion in epoxy resins, Part 1: Non-fickian sorption processes." *Polym Eng Sci.*, 25, **1985**: 521 - 528.
- Wood C., Bradley W.L.,. "Determination of the effect of seawater on the interfacial strength of an interlayer e-glass/graphite/epoxy composite by in-situ observation of transverse cracking in an environmental SEM." *Compos. Sci. Technol.*, 57, **1997**: 1033 - 1043.
- Wood D., Loveday P. "Ultrasonic detection of cracks in uniaxial glass fibre rods." *Fifth South African Conference on Computational and Applied Mechanics* (p. 11). Pretoria: South African Conference on Computational and Applied Mechanics (SACAM), **2006**.
- Worden K., Manson G., Allman D. "Experimental validation of a structural health monitoring methodology: Part I. Novelty detection on a laboratory structure." *Journal of Sound and Vibration*, 259 (2), **2003**: 323 - 343.
- Wróbel G., Pawlak S. "Ultrasonic evaluation of the fibre content in glass/epoxy composites." *JAMME*, 18(1-2), **2006**: 187-190.

- Wu H.F., Dwight D.W., Huff N.T., "Effects of silane coupling agents on the interphase and performance of glass-fiber-reinforced polymer composites." *Compos Sci Technol*, 57:, **1997**: 975–83.
- Wu L., Murphy K., Karbhari V.M., Zhang J.S., "Short-term effects of sea water on E-glass/vinylester composites." *J. Appl. Polym. Sci.*, 84(14), **2002**: 2760-2767.
- Xie Y., Hill C.A.S., Xiao Z., Militz H., Mai C. "Silane coupling agents used for natural fiber/polymer composites: A review." *Composites: Part A*, 41, **2010**: 806-819.
- Yang K., Gu M., Jin Y., Mu G., Pan X., "Influence of surface treated multi-walled carbon nanotubes on cure behavior of epoxy nanocomposites." *Composites: Part A*, 39(10), **2008**: 1670-1678.
- Yang Q., Xian G., Karbhari V.M., "Hygrothermal ageing of an epoxy adhesive used in FRP strengthening of concrete." *J. Appl. Polym. Sci.*, 107, **2008**: 2607-2617.
- Ye H., Jie T., Hongbo Z., Cheng Q., Yiyu F., Jie L. "Functionalized Few-Walled Carbon Nanotubes for Mechanical Reinforcement of Polymeric Composites." *ACSNANO Vol.3 No. 5*, April 27, **2009**: 1057-1062.
- Yeh M.K., Hsieh T.H., Tai N.H. "Fabrication and mechanical properties of multi-walled carbon nanotubes/epoxy nanocomposites." *Mater Sci Eng A*, 483-484, **2008**: 289 - 292.
- Young S.S., Jae R.Y. "Influence of dispersion states of carbon nanotube on physical properties of epoxy nanocomposites." *Carbon*, 43, **2005**: 1378 - 1385.
- Yu M-F., Lourie O., Dyer M.J., Moloni K., Kelly T.F., Ruoff R.S. "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load." *Science Vol. 287 No. 5453*, **2000**: 637-640.
- Yu B., Jiang Z., Tang X-Z., Yue C.Y., Yang J., "Enhanced interphase between epoxy matrix and carbon fiber with carbon nanotube-modified silane coating." *Composites Science and Technology*, 99, **2014**: 131-140.
- Zafar A., Bertocco F., Thomsen J.S., Rauhe J.C. "Investigation of the long term effects of moisture on carbon fiber and epoxy matrix composites." *Composites Science and Technology*, 72, **2012**: 656-666.
- Zhang Q.H., Liu J.W., Sager R., Dai L., Baur J. "Hierarchical composites of carbon nanotubes on carbon fiber: Influence of growth condition on fiber tensile properties." *Compos Sci. Technol.*, 69(5), **2009**: 594 - 601.
- Zhang J., Zhuang R., Liu J., Mader E., Heinrich G., Gao S. "Functional interphases with multi-walled carbon nanotubes in glass fiber/epoxy composites." *Carbon*, 48(8), **2010**: 2273-2281.
- Zhao Y., Qui J., Feng H., Zhang M. "The interfacial modification of rice straw fiber reinforced poly(butylene succinate) composites: Effect of aminosilane with different alkoxy groups." *Journal of applied polymer science*, 125(4), **2012**: 3211-3220.
- Zhou H.W., Mishnaevsky Jr. L., Yi H.Y., Liu Y.Q., Hu W., Warriar A., Dai G.M., "Carbon fiber/carbon nanotube reinforced composites: Effect of CNT distribution on shear strength." *Composites Part B*, 88, **2016**: 201-211.
- Zhou J., Lucas J.P. "Hygrothermal effects of epoxy resin. Part II: variations of glass transition temperature." *Polymer*, 40, **1999**: 5513-22.

Zhou Y., Farhana P., Lewis L., Jeelani S. "Experimental study on the thermal and mechanical properties of multi-walled carbon nanotube reinforced epoxy." *Materials Science and Engineering*, 452, **2007**: 657-64.

Zhou T., Wang X., Liu X., Xiong D. "Influence of multi-walled carbon nanotubes on the cure behavior of epoxy-imidazole system." *Carbon*, 47(4), **2009**: 1112-1118.

Zhou T., Wang X., Liu X.H., Lai J.Z. "Effect of silane treatment of carboxylic-functionalized multi-walled carbon nanotubes on the thermal properties of epoxy nanocomposites." *eXpress Polymers Letters*, Vol. 4, No. 4, **2010**: 217 - 226.

Zhu J., Peng H., Rodriguez_Macais F., Margrave J.L., Khabashesku V.N., Imam A.M., Lozano K., Barrera E.V. "Reinforcing Epoxy Polymer Composites Through Covalent Integration of Functionalized Nanotubes." *Adv. Funct. Mater*, 14, **2004**: 643-648

Zinck P., Mader E., Gerard J.F. "Role of silane coupling agent and polymeric film former for tailoring glass fiber sizings from tensile strength measurements." *J. Mater. Sci.*, 36 (21), **2001**: 5245-5252.

Zulfi NH M., Bakar A. Abu, Chow WS. "Mechanical and water absorption behaviors of carbon nanotube reinforced epoxy/glass fiber laminates." *Journal of Reinforced Plastics and Composites*, 0(00), **2013**: 1-7.