MOISTURE DIFFUSION AND THERMAL AGING EFFECTS IN GLASS FIBRE REINFORCED POLYMER EPOXY LAMINATES

A
Thesis Report

Submitted in partial fulfillment of the requirement for the award of degree

MASTER OF ENGINEERING
in
PRODUCTION AND INDUSTRIAL ENGINEERING

Submitted By
Vishwasrao Bajirao Patil
(Roll No. 820982006)

Under Guidance of

Mr. BIKRAMJIT SHARMA
Assistant Professor
Deptt. Of Mechanical Engg.
Thapar University, Patiala

Dr. RAJEEV MEHTA
Head & Associate Prof.
Deptt. Of Chemical Engg.
Thapar University, Patiala

MECHANICAL ENGINEERING DEPARTMENT
THAPAR UNIVERSITY, PATIALA-147004, INDIA
(Declared as Deemed-to-be university u/s 3 of the UGC Act, 1956)

CERTIFICATE

This is to certify that the thesis titled "**Moisture diffusion and thermal aging effects in Glass fiber reinforced polymer nano-composites laminates"** being submitted by "**Mr.Vishwasrao Bajirao Patil, Registration No-820982006"** in partial fulfillment of the requirement for the award of degree MASTER OF ENGINEERING (PRODUCTION AND INDUSTRIAL ENGINEERING) at THAPAR UNIVERSITY, PATIALA is a bonafide work carried out by me and no part of this seminar has been submitted before for award of degree.

Date: 07.01.2013

V Patil
(Vishwasrao Bajirao Patil)

This is to certify that the above declaration made by the student concern is correct to the best of my knowledge and belief.

Bikramjit Sharma
Mr. BIKRAMJIT SHARMA
Assistant Professor
Deptt. of Mechanical Engg.
Thapar University, Patiala

Rajeev Mehta
Dr. RAJEEV MEHTA
Head & Associate Prof.
Deptt. of Chemical Engg.
Thapar University, Patiala

Countersigned by:

21/1/13
Dr. AJAY BATISH
Head & Prof.
Deptt. of Mechanical Engg.
Thapar University, Patiala

Dr. S.K. MOHAPATRA
Dean Academic Affairs
Thapar University, Patiala

ACKNOWLEDGEMENT

I am highly grateful to the authorities of Thapar University, Patiala for providing this opportunity to carry out the thesis seminar report work.

I would like to express a deep sense of gratitude and thank profusely to my thesis guide **Mr. Bikramjit Sharma, Assistant Professor, Mechanical Engineering Department and Dr. Rajeev Mehta, H.O.D, Chemical Engineering Department** for their sincere & invaluable guidance and suggestions which inspired me to submit thesis report in the present form.

I am highly thankful to Mr. Toesh (Ph.D Scholar in Chemical Engineering Department) for his continuous support and helping in conducting tensile & flexural testing. I heartily thank to Mr.Kuldeep of Textile Technology Dept., IIT Delhi for conducting SEM test and Mr. Jagtar Singh and Mr. Dinesh Kumar Sharma for helping me in conducting the tests on T.E.M. machine and XRD machine.

I am also thankful to other faculty members and all the workshop staff of Mechanical Engineering Department and Chemical Engineering Department, Thapar University, Patiala for their valuable support.

I would also like to thank and acknowledge BASF Construction Chemicals (India) Private Limited and Connell Bros. Mumbai for supplying us generously with E-Glass Fibre sheet, M Brace epoxy (Base and hardener) and Clay (Cloisite 30B) etc. for this experimentation.

My special thanks are due to my family members, friends and my office colleagues who constantly encouraged me to complete this study.

Vishwasrao Bajirao Patil

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Polymeric composites are inherently sensitive to environmental factors such as temperature, exposure to liquids, gases, electrical fields and radiation. Static and dynamic mechanical loads can interact with environmental parameters and accelerate the degradation process. Moisture absorption behavior of Polymer epoxy Nano composites (PNC) in water and saline conditions is a complex phenomenon. Moisture diffusion weakens the fiber/matrix interface which leads deterioration of Mechanical properties. Hygrothermic aging of two configurations: (i) E-glass fiber epoxy laminate (EEE) (ii) E-glass fiber lamina sandwitched between C-glass fiber laminas (CEC) for neat and 2% clay loading were studied for their suitability in humid applications. The specimens were exposed to water and saline environment at 45^{o} C temp for duration of 7 day, 15 day and 30 days. The specimens were periodically weighted for moisture absorption and tested Mechanical properties (Ultimate tensile strength, flexural strength) & Microscopic behavior. The maximum moisture absorption was observed for 0% EEE epoxy laminates and minimum for 2% CEC epoxy laminates. Diffusion mechanism was studied on the basis of Ficks law of diffusion. It was found that diffusion coefficient (D) was largest for 0% EEE and lowest for 2% CEC laminates. Water absorption increases with increase in immersion time for all the samples. Water uptake is rapid and linear in the beginning of exposure after which it slows down and reaches saturation level. All Glass fiber epoxy laminates have tendency to absorb more water in saline environment. Although all the nanocomposites undergo degradation and lowers in mechanical properties subjected to hygrothermic aging, CEC laminates shows better results in Tensile and flexural strength than three ply E glass fiber epoxy laminates. The experimental observations were tested and confirmed by SEM.

CONTENTS

Chapter-I

INTRODUCTION

The materials used for various engineering purposes are of two type's i.e. organic and inorganic material. Organic substances are mostly derived from living organisms which contains carbon as one constituent. Some examples of organic materials are Animal Hides (leather), wood, oil (petroleum), several chemicals, paints, man-made polymers and natural resins. Polymer composites made by reinforcing polymer with different fibers have been the mainstay of high performance structural material for aerospace, defence, marine, automobile, civil, infrastructure, safety goods etc. With the advent of Nanotechnology, it has become possible to control and manipulate materials at the nanoscale (particle size from 1 to 100 nm, where 1 nm=1 billionth of a meter) to create new materials and structures that have novel properties due to increased surface area (being very small size of material). Materials with feature on the scale nanometres (10^{-9}meter) often have properties dramatically different from their bulk-scale counterparts [Sakaki, 1994]. One of the major factors, which alter these properties, is the increase in the ratio of surface area to volume. As the surface area of a particle increases exponentially, creating more sites for bonding, catalysis or reaction with surroundings material, resulting in improved properties such as increased strength or chemical or heat resistance. Hence, due to the high surface-to volume ratio associated with nanometer sized particles it is possible to control the fundamental properties of materials through the surface/size effect.

1.1 Polymer Nanocomposites (PNC) -Nanocomposites are composites in which the interphases dominate the composite properties because of the very small size of the components—100 nm or less. In mechanical terms, nanocomposites differ from conventional composites due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibers (e.g. carbon nanotubes or electrospun fibers). Polymer nanocomposites (PNC) are polymers (thermoplastics, thermosets, elastomers) that have been reinforced with small quantities (less than 5% by weight) of nano-sized particles. Molecular interaction between polymer and nanofillers do not possess. The difference from

traditional composites and filled plastic is that, the PNC is having uniform dispersion of nanoparticles in polymer matrix produces ultra- large interfacial area per volume between the nanoparticle and the host polymer. The most commonly used nano fillers are:

- Manomorillonite organoclays (MMT)
- Carbon nanofibers (CNFs)
- Carbon nanotubes (CNTs)
- Metallic nanoparticles
- Others

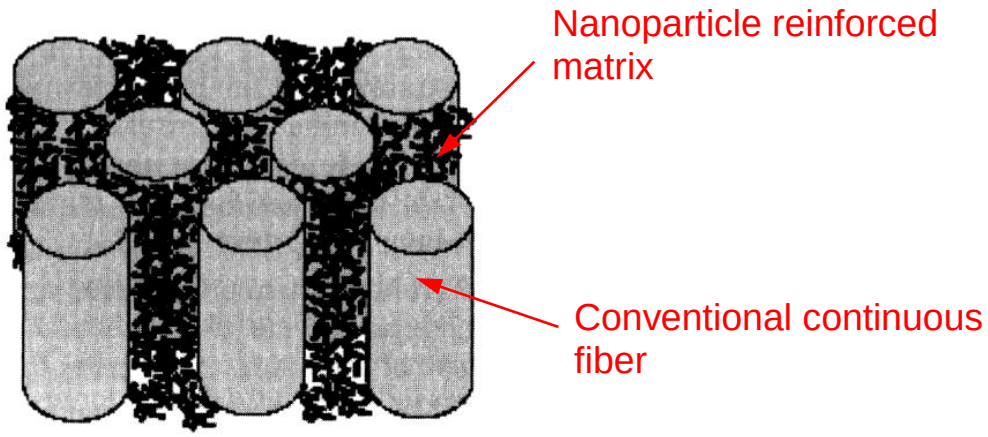


Fig 1.1- Fiber Reinforced Nanocomposite [1]

1.2.1 Epoxy Nanocomposites

Epoxy, also known as polyepoxide, is a thermosetting polymer formed from reaction of an epoxide 'resin' with polyamine 'hardener'. Epoxy has a wide range of applications. The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements (although polyester, vinyl ester and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. Many properties of epoxies can be modified (for example silver-filled epoxies with good electrical conductivity are available, although epoxies are typically electrically insulating). Variations offering high thermal insulation or thermal conductivity combined with high electrical resistance for electronics applications.

1.2.2 Clay Nanoparticales

Clay such as smectic clays (e.g. montmorillonite) are incorporated into polymers (as a nanoparticals) to form resulting polymer nanocomposite which possess unique electrical, mechanical and optical properties. The clay as filler is expected to strengthen the mechanical properties and Fire retardancy, barrier resistance and ion conductivity of PU even upon lower loading of clay as a filler. Polymer/clay nanocomposites comprise organic/inorganic hybrid polymer matrices containing platelet-shaped clay particles that have sizes of the order of a few nanometers thick and several hundred nanometer long. Partly because of their aspect ratios and high surface areas, the clay particles, if properly dispersed in the polymer matrix at a loading level of 1 to 5 wt. %, impart unique combinations of physical and chemical properties. Relative to the unmodified polymer, the polymer/clay nanocomposites may exhibit improvements in strength, modulus, and toughness, tear, radiation, fire resistance, and lower thermal expansion and permeability to gases while retaining a high degree of optical transparency [www.techbriefs.com].

According to the structure three different types of clay-polymer composites can be distinguished.

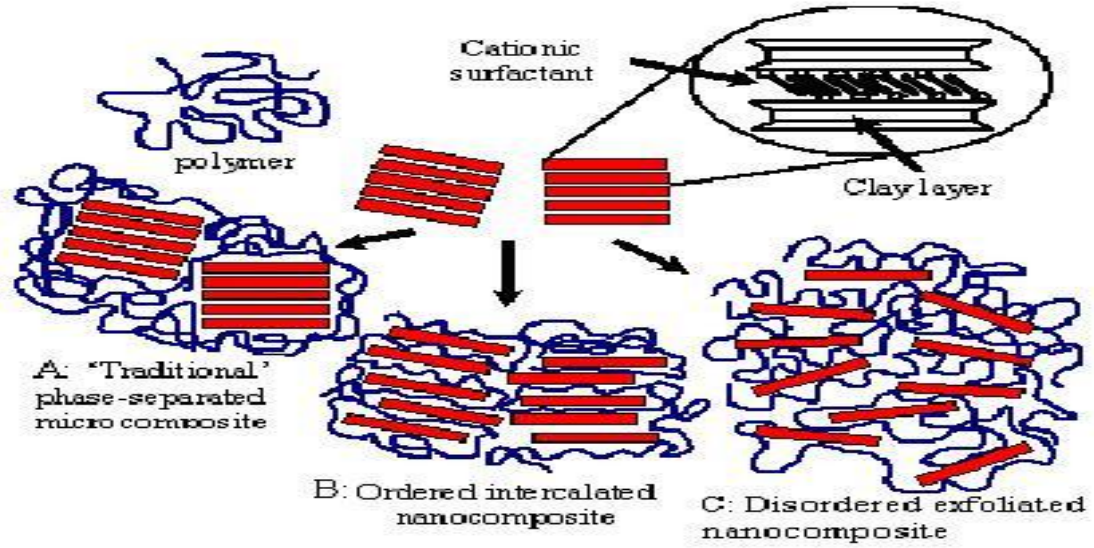


Figure 1. 2. Three idealized structures of polymer-clay composites [1]

- When the matrix polymer chains are unable to penetrate between the layers of the silicate particles a conventional composite is formed.

- Intercalated structures are formed when one or more polymer chains intercalate between the layers. Hereby the interlayer spacing is increased but the ordered layer structure of the clay particles is retained as can be observed by wide angle X-ray diffraction (XRD).
- In exfoliated composites the clay particles are completely delaminated and the silicate layers do not show any periodicity in their arrangement.

1.3 Glass Fiber

Glass fiber is a lightweight, extremely strong, and robust material. Strength properties are lower than carbon fiber and it is less stiff, the material is typically far less brittle and is much less expensive. Its bulk strength and weight properties are also very favorable when compared to metals, and it can be easily formed using molding processes. Glass fibers are used for preparing Fiber-reinforced polymer (FRP) which a composite material made of a polymer matrix reinforced with fibers

Types of Glass Fibers-

E-glass – Strong and low cost, but modulus is less than other (500,000 psi) Alumina-calcium-borosilicate glasses with a maximum alkali content of 2% w/w used as a general purpose reinforcement where strength and high electrical resistivity are required.

E-CR Glass – Acid resistance with the reinforcing characteristics of E-glass.

AR Glass – Alkali resistant glasses composed of alkali zirconium silicates, Developed for use in use in cement and concrete. Mainly used for GRC (Glass reinforced Cement) roofing and sheeting panels.

C glass. – Calcium borosilicate glasses used for their exceptional stability in acidic environments. Also known as corrosion and chemical resistant glass fibers. To protect against water erosion, a moisture-resistant coating such as a silane compound is coated onto the fibers during manufacturing. Adding resin during composite formation provides additional protection. C-Glass fibers are used for manufacturing storage tanks, pipes and other chemical resistant equipment Such as application in surface mats, glass flakes for coatings and acid resistant surface cloth.

D glass. – Borosilicate glasses with low dielectric constant used for radomes and other specialty applications requiring permeability to electromagnetic waves.

E-CR Glass. – Calcium aluminosilicate glasses with a maximum alkali content of 2% w/w used where acid corrosion resistivity is required in addition to strength and electrical resistivity. Introduced in 1980.

R-glass. – Calcium aluminosilicate glasses with higher strength and temperature resistance.

S-glass. – Magnesium aluminosilicate glasses used for textile substrates or reinforcement in composite structural applications, which require high strength, modulus and durability under conditions of extreme temperature of corrosive environments.

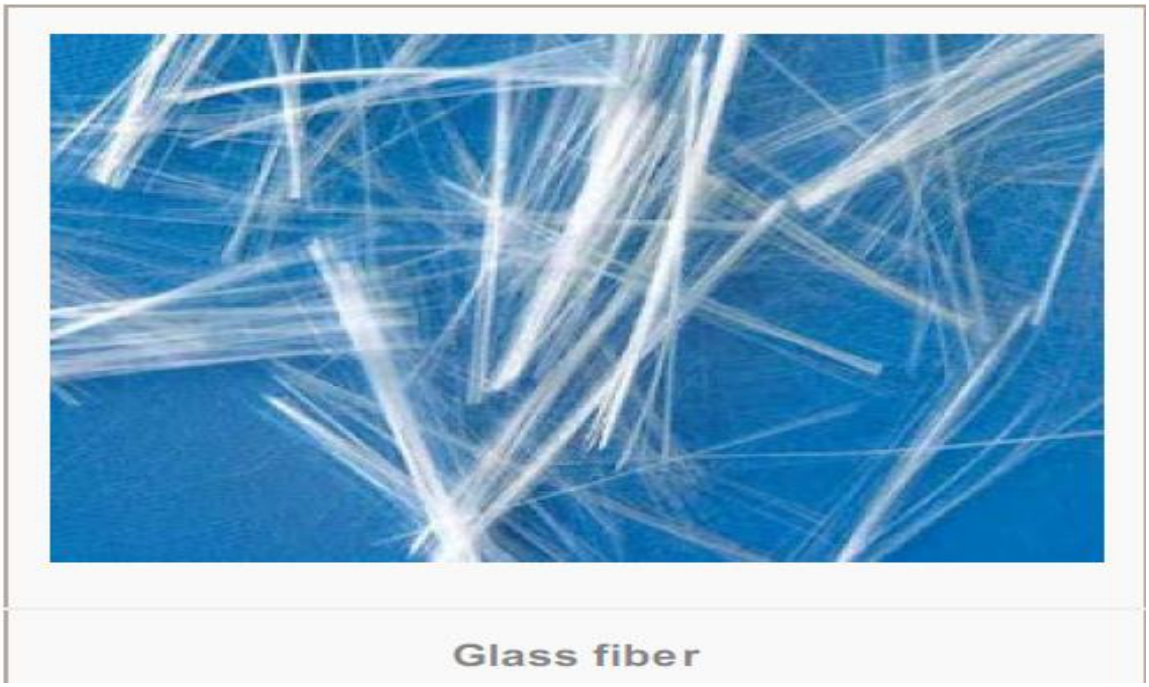


Fig.1.3 &1.4 Commercially available glass fibers [4]

Letter designation Property or characteristic

E - Electrical Low electrical conductivity

S - Strength High strength

C - Chemical High chemical durability

M - Modulus High stiffness

A - Alkali High alkali or soda lime glass

D - Dielectric Low dielectric constant

1.4 Environmental effects on Fiber Composites

Composite usage has increased dramatically over the last three decades due to the advantages of light weight, specific strength and stiffness, dimensional stability, tailorability of properties such as coefficient of thermal expansion and high thermal conductivity. But the performance of these materials is affected by environments to which they are subjected to during operation. When a fiber reinforced material is exposed to a hygrothermal environment and mechanical loads, changes in material properties are expected. These changes in material properties are connected to an irreversible material degradation. The moisture may affect the laminates through chemical changes such as relaxation and oxidation of the matrix material. A cyclic moisture environment exposed to a laminate may cause damage such as debonding at fiber/matrix interfaces and continuous cracks. Water acts as a plasticizer when absorbed by the matrix, softening the material and reducing some properties of the laminate. Moisture may also migrate along the fiber-matrix interface, affecting the adhesion. Moisture in composites reduces matrix-domi-nated properties, such as transverse strength, fracture toughness and impact resistance. Lowering of the glass transition temperature may also occur in epoxy and polyimide resins with an increase in absorbed moisture. Debonding can occur due to formation of dis-continuous bubbles and cracking in the matrix.

For an undamaged material, well-accepted moisture transportation models are available. The most common models for the transportation of moisture in undamaged polymeric composite materials are Fickian diffusion and Langmuir diffusion. If the material contains cracks that

significantly affect the moisture uptake, then the original laws of Fickian and Langmuir are no longer valid for the whole laminate, but locally they still work.

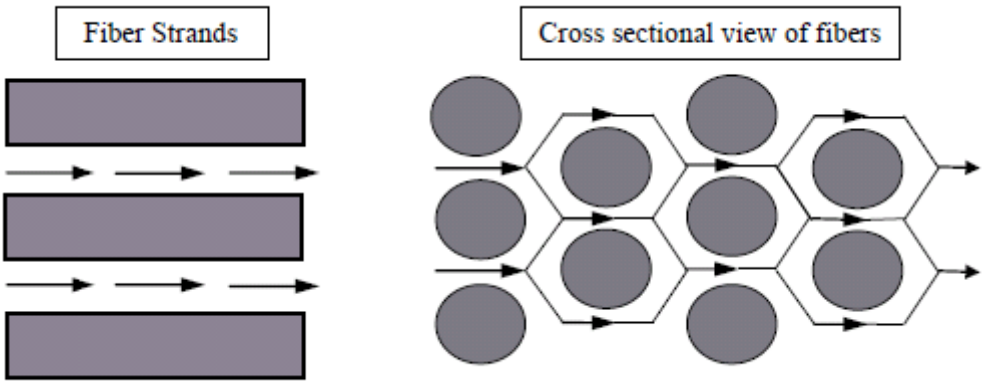


Fig. 1.5 Diffusion path of moisture into composite thickness direction

[2]

1.5 E-Glass Fiber surface Treatment

Composition of E-glass used for fiber manufacture in percent weight.

Chemical	Composition (%wt)
SiO_2	52.4
Al_3O_3, Fe_2O_3	14.4
CaO	17.2
MgO	4.6
Na_2O, K_2O	0.8
Ba_2O_3	10.6

AMANDA KAY DAVIS submitted Thesis on Influence of surface treatment and humidity on strength of E-glass fiber bundles submitted to B.S., University of Illinois, 1997. He had performed four types of surface treatment on E Glass Fiber to investigate the influence of surface treatment and humidity on the tensile strength of E-glass and presented experimental data for E-glass fiber bundles. Four types of commercial surface treatment were tested at four levels of humidity. The four type surface treatment performed on E Glass Fibers were 1. Starch 2. Starch and silane 3. Starch and wax 4. Epoxy . He had immersed E Glass Fiber Bundle in the separate coating baths of these four coating these four types of fiber bundles were tested after conditioning in four different levels of humidity: 10, 40, 80, and 100% RH. for surface treatment and humidity

level. The comparative study reveals that the starch/silane surface treatment had the highest peak load at each humidity level, even with a drop in average peak load at 100% RH. The silane added to the starch chemistry prevents moisture absorption throughout the life of the fibers. tensile strength values were also measured for saline and starch coated fibers at low humidity levels .The wax additive in Starch and wax coated E Glass Fiber serves as a lubricant that protects the fibers from surface damage. The average peak load for the wax treated fibers decreased dramatically when soaked at 100% RH. Although the wax effectively prevents surface damage at low humidity, it does not protect against moisture damage at high humidity levels. Epoxy coated E Glass Fibers had the lowest average peak load at each humidity level and due to epoxy coating on E Glass Fibers there was increase in the surface roughness and caused a decrease in tensile strength due to increased contact abrasion. A thin coating applied to the E Glass fibers to protect the surface from damage, to lubricate the fibers during manufacturing, to minimize static, or to enhance interfacial bonding with a binder or matrix. For example, wax coatings lubricate during weaving, while epoxy sizes enhance interfacial adhesion. Silane surface treatments are commonly used to promote adhesion and protect against moisture damage. The silane coupling agent also keeps water molecules in an equilibrium reaction outside of the glass so the water will not react with the glass fiber .

CHAPTER 2

LITERATURE REVIEW

Fatemeh Ravari et al. (2012) studied ageing behaviour of low viscosity epoxy polymer by various techniques and effect of addition of nonoalumina at various concentrations on corrosive resistance. The specimens were prepared by of Epoxy comprising of Glycerol diglycidyl ether 3,3-dimethyl glutaric anhydride (DGA) hardener and nanoalumina (1, 3, 5,10 & 15 phr), ultrasonic assisted dispersion treatment was employed for 60 min to produce homogenous mixture. The solution was casted on a Teflon mold and then placed in a vacuum oven for 30 min at 120^0C to remove air bubbles. Samples were cured at 130^0C for 2 h. Water and ageing of the sample were studied by exposing samples to distilled water up to 50 days. The anticorrosion performances of the samples were studied by Electrochemical Impedance Spectroscopy (EIS) technique. EIS measurements were also performed on 0, 10, 30, 40, and 50 days submerged neat epoxy and nanocomposite (10 phr) samples for comparison together. Resistance of the neat epoxy and nanocomposite (10 phr) systems was also examined under influence of ageing with sulphuric acid aqueous solutions (10%W). Visual and microscopic observations showed that based on 50 days water immersion, that nano-reinforced GDE was better than the neat epoxy. Decrease in cross-linking density of the GDE matrix reinforced with nanoalumina after exposure to the corrosive electrolyte, were considerably lower than the neat GDE system. Water uptake decreased for the GDE nanocomposite owing to the presence of nanoalumina. The highest improvement was observed for the sample which was reinforced by 10 phr nanoalumina. The surface topography and morphology of the nanocomposites were studied using AFM. AFM studies revealed that the nanoparticles and water ageing cause an increase in the surface roughness of the nanocomposite. It was found that nanoalumina reinforced epoxy display higher strength and strain to failure than the neat system for both emersed and unimersed sample.

H. Alamri et al. (2012) fabricated RCF reinforced epoxy composites with different fiber contents (19, 28, 40 and 46) wt%. Recycled cellulose fiber (RCF) grade 200 GSM and 200 mm thickness (fibres diameter between 5 mm to 10 mm and several micrometers in length) sheet was

used as reinforcement for the fabrication of epoxy-matrix composites. General purpose low viscosity epoxy resin (FR-251) and epoxy hardener (FR-251) was used as a matrix. Composite samples were prepared by initially pre-drying the paper sheets for 60 min at 70^0C, and then fully immersing them into the epoxy system until they became entirely wetted by the resin. After that, the epoxy-soaked RCF sheets were carefully laid down in a closed silicone mould under 8.2 KPa compressive pressure and left for 24 h to cure at room temperature. RCF/epoxy composites were fabricated with different weight percentages of consisted of both flexural and shear failure modes. Composites loaded with higher fiber content had better fiber-matrix interfacial bonding than those loaded with lower fiber content. Water absorption was observed to increase with increasing fiber content due to hydrophilic nature of cellulose fibers. Exposure to moisture for two weeks caused a reduction in flexural strength, flexural modulus and fracture toughness due to the degradation of bonding at the fiber–matrix interfaces. The mechanical properties (flexural strength, flexural modulus, fracture toughness and impact toughness) increases as the fiber content increased. The stress-strain curves showed that the failure mode of the RCF reinforced epoxy composites However, impact strength was found to increase slightly after water absorption. The effect of water absorption on mechanical properties was more pronounced at high fiber content than at low fiber content

A. Alhuthali et al. (2011) studied effect of nano-clay on water absorption, mechanical, flammability and thermal properties of eco-nanocomposites. The material used for preparing sample was Recycled cellulose fiber sheets (RCFs) of grade 80GSM, 100 micrometer thickness, general purpose vinyl ester resin and organoclay (Cloisite 30B), Pure polymer samples was prepared baseline data. The eco-nanocomposites were prepared using nanocomposite mixtures containing different concentrations 1%, 3%, and 5%, of Cloisite 30B . Nanoclay was first dried for 60 minutes at 150C, and then mixed with vinyl ester resin for 30 min using high speed electrical-mixer. The mixtures were then left under (150 KPa) to remove air bubbles. Next, the mixtures were reinforced with the same percentage of RCFs sheets (40 wt.%). The sheets then were fully soaked in the mixtures and pressed together under 20 kg and under vacuum of (150 kPa) for two hours. Finally, the samples were left to cure at room temperature for 24 hours. Microstructure examination, Water uptake test , Fourier transform infrared spectroscopy (FTIR) and mechanical tests was conducted on the specimens. XRD patterns for both nanoclay and clay nanocomposites shows sharp reflection peak is demonstrated for Cloisite 30B corresponding to interlaying spacing of 1.8 nm. Different results were revealed in the XRD of nanocomposites

with 5 wt.% nanoclay which is shifting to a broad, weak lower diffraction peak and interlaying spacing of 2.1 nm. An intercalated nanocomposite structure was the result evident from entrance of matrix polymer into nanoclay interlayer spacing and increased d-spacing.at 1 wt% and 3 wt.% nanoclay there was no reflection peak for the XRD patterns of the composites. Nanoclay was found to effectively decrease the water uptake in eco-nanocomposites with 5% loading giving more favorable results compared to 1% and 3%. Strength properties were also found to be enhanced due to the reinforcing effect of both RCF and nanoclay. With weight percentage of nanoclay particles, flexural modulus increased except for the 5% NC specimens in which high void content leads to a decreased flexural modulus. However, nanoclay addition resulted in samples which were brittle due to the nanoclay's effect on the fiber-matrix adhesion so the toughness were lower. Nanoclay addition increased both the thermal stability and fire-resisting properties of the composites.

Hossain *et al*. (2011) studied the effect of seawater on the degradation of mechanical properties of conventional and nanophased carbon-epoxy composites was investigated. Epoxy resin was modified using 1 wt.%, 2 wt.%, and 3 wt.% nanoclay. Carbon-epoxy composites were fabricated by vacuum assisted resin transfer molding process and compared with neat samples with and without exposure to seawater. Nanoclay was dispersed into matrix by using magnetic stirring. Mechanical characterization performed through three point bending tests showed that 2 wt.% nanoclay loading was optimum. Flexural strength and modulus were increased by 25% and 12.51%, respectively, compared to neat system for samples not exposed to seawater. Flexure samples exposed to the seawater for 30, 60, and 180-day periods revealed that samples with nanoclay retained better mechanical properties compared to neat samples. After 30-day exposure to seawater, there was no significant reduction in the strength and modulus. However, flexural strength was reduced by 10.24%, 7.08%, 5.28%, and 7.13% for neat, 1 wt.%, 2 wt.%, and 3 wt.% nanoclay-infused samples, respectively, after the samples were exposed to seawater for 180-day. At the same time flexural modulus was reduced by 12.61%, 7.16%, 4.59%, and 6.11%, respectively. From scanning electron microscopy (SEM) studies, it was found that failure occurred due to delimitation and initiated from the compression side. Nanophased composites exhibited better bonding between fiber and matrix. SEM micrographs also revealed that both unconditioned and conditioned nanophased epoxy, which produce relatively rougher fracture surfaces compared to neat samples. Optical microscopy study revealed no significant physical change in outer surfaces of the samples conditioned up to a 90-day period.

Zainuddin *et al*. (2010) was shown here that E-glass epoxy fiber reinforced composite was sensitive to environmental conditioning especially under hot-wet conditions. The weight gain was higher for all the wet conditions samples exposed to elevated temperatures. Addition of 1–2 wt.% of nanoclay decreased the weight gain. Flexural properties were found to degrade with increase in time. 2 wt% GFRP composites showed enhancement in properties under all conditions over neat counterparts. In some cases, samples subjected to hot dry condition at 60^{0}C showed increase in properties over room temperature conditioned samples. Scanning electron micrographs provided clear evidence of the effects of nanoclay, elevated temperature and moisture absorption. Enhancement in interfacial bonding was observed in 2wt.% composite samples, both at room temperature and hot-wet conditioning.

Sreejith Muthirakkal et al.(2009) studied the effects of temperature and moisture on the flexural strength (FS), ultimate tensile strength (UTS) and interlaminar shear strength (ILSS) of the polymer matrix composites using glass or carbon fibres as reinforcements and epoxy or vinylester as resin systems. Water uptake of polymer matrix composites (epoxy/glass, epoxy/carbon, vinylester/glass and vinylester/carbon) was studied by exposure at 50°C, 60°C and 70°C temperature and 95% RH in an environmental testing chamber for a maximum duration of 170 days. The maximum moisture uptake was the least for vinylester/carbon samples and highest for epoxy/glass composite samples. It was observed that moisture absorption increased with increase in temperature in all the cases. The composites degradation in the periods subsequent to saturation was much less than that of pre-saturation period. The better performance of vinylester based samples was attributed to its chemical stability and the gel coat effect. Vinylester/carbon samples were found superior to epoxy/carbon ones because of the lower degradation levels exhibited by the former in ultimate tensile strength, flexural strength and interlaminar shear strength in all the test conditions. Temperature increased the matrix degradation and hence more fiber pull-out was observed in 70°C conditioned specimens. The worst affected parameter in all the experimental conditions was ultimate tensile strength, followed by flexural strength and interlaminar shear strength, which was observed commonly in all the four material composite systems.

Ramirez *et al.* (2008) investigated the degradation of polymer matrix composites for naval application subjected to distilled and sea water. Three types of fibers: T700 carbon fibers, AS4

carbon fibers and E-glass fibers were combined with (i) MAS epoxy, and vinyl esters (ii) VE D411(ii) VE D8084 (iii) VE H922L. Resin specimens were made from VE D411, VE D8084, VE H922L, and MAS epoxy. Single fiber fragmentation test (SFFT) was used to determine the F/M interface shear strength and extent of F/M debonding. The following fiber and matrix combinations were studied using the SFFT: T700/VE D411, T700/VE D8084, T700/MAS epoxy, AS4/VE H922L, E-glass/VE D8084, and E-glass/MAS epoxy. Unidirectional composites were examined using transverse tensile and transverse flexure tests. Unidirectional composites were made from T700/VE D411, T700/VE D8084 and T700/epoxy. Laminates consisting of four plies were fabricated using vacuum-assisted resin transfer molding at room temperature (VARTM) and cured for 24 h. The specimens were immersed in distilled water at room temperature (RT) and seawater at RT, 40^0 and 60^0C. For studying the weight gain, the weight change was periodically monitored. It was observed that neat epoxy absorbed much more water than neat vinyl ester. The vinyl ester matrix composites absorbed more moisture than the neat resins whereas epoxy composites absorbed less water than neat epoxy. The flexure test performed on the neat resins showed that the vinyl ester matrices were not significantly affected by exposure to water while the strength of the epoxy was reduced by a factor of 2. Single fiber fragmentation testing revealed large extents of F/M debonding and substantial reductions in the F/M interface shear strength of all systems after exposure to water. The E-glass systems performed better than the carbon systems in terms of retention of the F/M interface shear strength and debonding, but it was found that E-glass fibers degrade by exposure to water, especially at elevated temperatures. Transverse tensile and flexure tests were performed on composite specimens to monitor the influence of F/M interface on macroscopic behavior. In addition, large reductions in transverse strength of the water immersed composites were experienced for all systems as a result of matrix and F/M interface degradation by water.

Berketis *et al.* (2007) investigated the matrix and fiber/matrix interfacial degradation of glass fiber composites subjected to water for very long time. Laminated composite plates were manufactured by the vacuum assisted resin transfer moulding technique. The resin used was the polyester (crystic 489 PA). This paper examines the durability of an isopthalic polyester resin reinforced with non-crimp glass fabrics in a hydrothermal environment for up to 30 months. The weight of the composite plates initially increased due to water diffusion up to month 14 and thereafter decreased due to material losses. The initial weight increase was due to diffusion of water into the specimens. Immersion in water also resulted in significant de-bonding of the

fiber/matrix interface, which allows water to penetrate the composite material by capillary action. The impacted plates were retested statically to determine residual compressive strengths for the assessment of damage tolerance. A new device was designed for the Computer Aided Inspection (CAI) tests that assured laminate failure by de-lamination propagation. The results of the CAI testing demonstrated a reduction in strength, due to hydrothermal exposure for each applied level of impact loading. Immersion time of 24 and 30 months.

Chow (2007) carried out X-ray diffraction, differential scanning calorimetry and water absorption tests on glass fiber reinforced epoxy nanocomposite. The clay used in this study was Nanomer I.30E which was added to diglycidyl ether bisphenol A and mixture was stirred at 100 rpm using mechanical stirrer till until all the OMMT was well dispersed in epoxy before the hardener was added. This mixture was then applied on glass fiber mat and laminated samples were prepared. Glass fiber reinforced neat epoxy matrix composites and neat epoxy specimens were also prepared by same route. The X-ray diffraction performed on the sample showed that the silicate platelets in the epoxy matrix were exfoliated. DSC results showed that the glass transition temperature (T_g) of epoxy was increased slightly in the presence of OMMT. The water absorption test performed as per ASTM D570. The specimens were immersed in water at 30^0C and weight gains were recorded by periodic removal of the specimens from water bath and weighing them. The water resistance properties of epoxy were found to be improved by addition of glass fiber and OMMT.

Wang *et al.* (2006) studied the hydrothermal effects on thermal and mechanical properties of neat epoxy and epoxy clay nanocomposite. The pristine clay modified epoxy nanocomposite was prepared using a "slurry compounding approach". The neat epoxy sample and epoxy clay nanocomposite were immersed in deionized water bath at 60^0C for a period of one month and were periodically subjected to wide angle X-ray scattering and transmission electron microscopy. Moisture absorption experiments showed less moisture uptake by neat epoxy in comparison to nanocomposite. To find the mechanical properties, uniaxial tensile test and three point bending tests were carried out on a set of six samples immersed in water up to 30 days. The mode I fracture toughness, as quantified by critical stress intensity factor was calculated using formula

$$K_{IC} = Y \frac{3PS\sqrt{a}}{2BW^2}$$

Where Y: shape factor, P: load at failure, S: strength of span, and a: crack length.

The values of K_{IC} and tensile modulus were found to be not influenced by moisture absorption. The tensile strength of neat epoxy was found to be constant, whereas that of epoxy/clay nanocomposite decreased after moisture absorption.

Chow *et al.* (2005) studied the water absorption and hygrothermal aging behavior of organomontmoiillonite (OMMT reinforced polyamide 6/polypropylene (PA6/PP ratio = 70/30)), with and without maleated PP (MAH-g-PP), at three different temperatures (30, 60, and 90^{o}C. The water absorption of the PA6/PP nanocomposites obeys the fickian law behavior. It was found that the equilibrium moisture content and the diffusion coefficients are dependent on the OMMT loading, MAH-g-PP concentration and immersion temperature tensile modulus and strength of PA6/PP nanocomposites deteriorated after being exposed to hygrothermal aging. Water acts as a plasticizer for the PA6/PP matrix and silicate layer of OMMT. These nanocomposites showed excellent retention ability and recovery properties under any immersion temperature. The MAH-g-pp enhances the resistance of the nanocomposites against water immersion.

Kornmann *et al.* (2005) synthesized and successfully used epoxy-layered silicate nanocomposites based on anhydride cured epoxy and octadecylamine modified fluorohectorite as matrix in glass-fiber-reinforced laminates by hand lay-up technique. The material used was the synthetic layered silicate Somasif ME-100. One hundred and twenty milli equivalents per 100 g of Somasif ME-100 of ocadecylamine were dispersed in deionized water at 80^{o}C. They had done the flexural tests on the laminates and indicated that the presence of silicate layers in the epoxy matrix leads to a flexural strength improvement of 27%. According to dynamic mechanical measurements, the presence of organosilicate causes a decrease of the glass transition temperature. The glass transition temperature decrease is apparently responsible for the larger water uptake observed in the nanocomposite.

Kim *et al.* (2005) studied moisture absorption and thermo-mechanical properties of epoxy modified with three different types of organoclays: a quaternary alkylamine modified montmorillonite (KH-MT®), a quaternary ammonium modified montmorillonite (closite 20A®) and an octadecylamine modified montmorillonite (I30P®). The resin and clay mixture was prepared using an ultrasonicator. For the moisture absorption test, specimens were hygrothermally treated in an environmental chamber at 85^{0}C for 25 days. It was seen that it took more time for moisture to diffuse into nanocomposites containing I30P and Closite organoclays

than KH-MT system. The moisture diffusivity of nanocomposites was found to be decreased with increasing clay content (3% and 5%). Moisture diffusivity was found to be decreased by 36% and 39% and 19% with 5wt% clay content of I30P, closite and KH-MT respectively as compared to neat epoxy resin. To study the effects of moisture on thermo-mechanical properties the authors carried out TMA on I30P nanocomposite and neat epoxy specimens. The images obtained showed that the presence of clay in epoxy matrix increased glass transition temperature significantly. The glass transition temperature of both epoxy and nanocomposite decreased linearly with increasing moisture content.

Kootsookos *et al*. (2003) investigated the effect of sea water immersion on glass- and carbon-fiber reinforced polymer composites. The materials studied were glass/polyester, carbon/polyester, glass/vinyl ester and carbon/vinyl ester composites used in marine structures. The composites were fabricated using the wet hand lay-up process into flat panels before curing at room temperature for several weeks. Some samples of glass/polyester and carbon/polyester composites were post cured by heating to 100 ^{0}C for two hours. The degree of resin cure as determined using differential scanning calorimetry (DSC) was 88% &100% for partially cured samples and fully cured samples respectively. The composites were immersed in seawater at a temperature of 30 ^{0}C for over two years and the mass change of specimen was compared. The mass change curves showed higher mass gain in glass polyester and glass/vinyl ester than their respective counterparts reinforced with carbon fibers. From the water uptake curves for the above material systems it was observed that the partially cured composites gained less mass than the fully cured materials. The flexural properties of composites as determined from four-point bend test method (ASTM D790) showed a small deterioration in flexure properties of polyester-based composites in comparison to vinyl ester based composites wherein the flexural modulus and strength decreased rapidly with increasing time and degraded by about 30% and 40-50% within a period of 3 days. The effect of seawater immersion on the durability of the fiber/matrix interphase of the composites was evaluated by mode I interlaminar fracture toughness testing performed in accordance to ASTM D5528. No significant change in interlaminar fracture toughness values were observed till apparent saturation time.

CHAPTER 3

RESEARCH PROBLEM AND METHODOLOGY

3.1 Gaps in literature

Polymeric composites are inherently sensitive to environmental factors such as temperature, exposure to liquids, gases, electrical fields and radiation. Static and dynamic mechanical loads can interact with environmental parameters and accelerate the degradation process. The incorporation of nanofillers in the matrix can reduce the liquid penetration into the matrix thus preventing matrix and fiber from degradation. A comparative study on strength degradation due to moisture diffusion in interply hybrid laminates, also reinforced with nanoclay, has not been performed so far. To fulfill the gap we considered two configurations: (i) E-glass fiber epoxy laminate (EEE) (ii) E-glass fiber lamina sandwitched between C-glass fiber laminas (CEC)

3.2 Research Objectives

1. Synthesis and characterization of fiber reinforced epoxy nanocomposites.
2. Degradation studies and analysis of results of laminates immersed in water and saline conditions.

CHAPTER 4

FABRICATION AND EXPERIMENTATION

4.1. Fabrication of specimen

4.1.1. Materials

Unidirectional E-glass fiber, C-Glass Fiber and M Brace a two part epoxy resin purchased from BASF Construction Chemicals (India) Private Limited. Organically modified nanoclay Closite 30B purchased from Connell Bros. Mumbai.

4.1.2. Specimen specifications

Commercially available glass fiber mat (E-glass fiber and/ C-Glass Fiber) had been used for making specimen. The sheets were placed for cutting the specimen. The specimen had been cut and prepared as per the assumed dimensions for tensile and bending tests respectively.

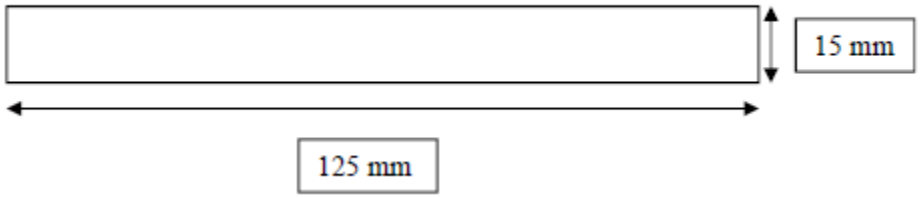
The assumed dimensions of specimens are shown below.

Table 4.1 Specimen specifications for testing as per ASTM D3039 and D790 for tensile and bending test respectively.

Sl.No.	Parameters for specimen	Specimens for tensile testing	Specimens for flexural testing
1	Length	125 mm	125 mm
2	Width	15 mm	13 mm
3	Thickness	5 mm	5 mm

4.1.2.1. Specimen dimensions

 For Tensile test



 For Bending test

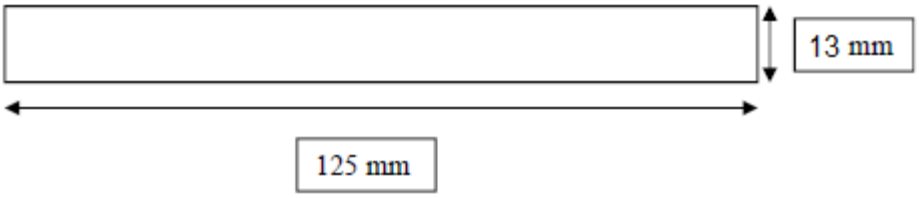


Fig 4.1 Sample specimen for tensile and bending test.

Fig 4.2 Sample for tensile and flexural testing

4.1.3. Cutting glass fiber sheet

For the experimentation, unidirectional E-glass fiber roll having 150 mm width having 0^0 fiber orientation woven with polymer fibers and C-glass chopped strand fiber purchased. The E Glass Fiber sheets were initially cut a square of length 500 mm.

Fig. 4.3 Uncoated C- glass fiber mat used for making specimen

Fig. 4.4 Uncoated glass fiber mat used for making specimen

4.1.4. Mixing of nanoclay into epoxy (base):

- Dehumidifying of Nano-clay : Nano clay of required proportion is taken and heated in vacuum environment at 60^{o} temperature in Vacuum oven for 2 hours period.
- Epoxy : Epoxy base blue colour thick fluid was poured in beaker and weight of epoxy was noted down.

Fig 4.5 Weighing of Nano-clay, epoxy and hardner using digital weigh 'METTLER TOLEDO'

- Mechanical stirring: Epoxy base is a blue colour thick fluid. It is quite difficult to mix nano clay into it manually. So we used a mechanical stirrer at 2000 RPM and an oil bath

for proper mixing of Nano clay (Fig. 4.5). Oil bath was used to heat up the epoxy to desired (60^{0}C) temperature, so the viscosity of epoxy base is reduced. Proper mechanical stirring of epoxy at this stage resulted better dispersion of clay (2% of weight of epoxy).

For making 0% Base samples:

Epoxy base blue colour is stirred at 500 RPM in an oil bath for 30 min and Hardner with designed proportion (40% of weight of epoxy) by M/s. BASF Chemicals is added slowly stirring and ensuring properly mixing of hardner with epoxy. (Fig 4.6)

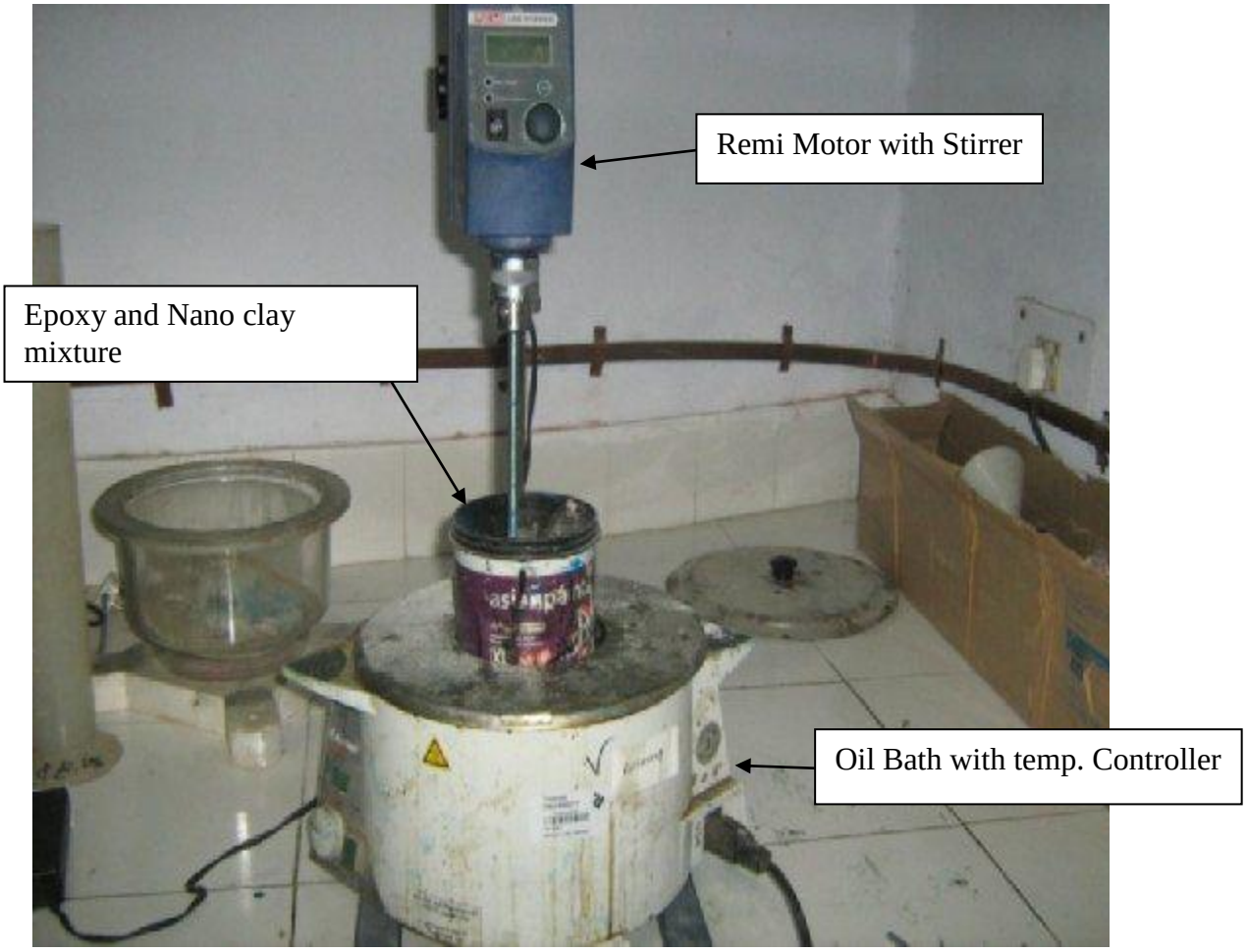


Fig 4.6 Mechanical stirrer for Mixing of epoxy and Nano-clay

Fig 4.7 Homogeneously Mixing of Epoxy and Hardner

 Ultrasonication after mechanical stirring: Sonication is the act of applying sound energy to agitate particles in a sample, for various purposes. In the laboratory, it is usually carried out using an ultrasonic bath or an ultrasonic probe, colloquially known as a sonicator. Sonication can be used to speed dissolution, by breaking intermolecular interactions. Sonication was done for evenly dispersing nanoparticles in liquids. After mechanical stirring of the epoxy solution container was placed into the ultrasonication bath for up to 3 hours. (Fig 4.7)

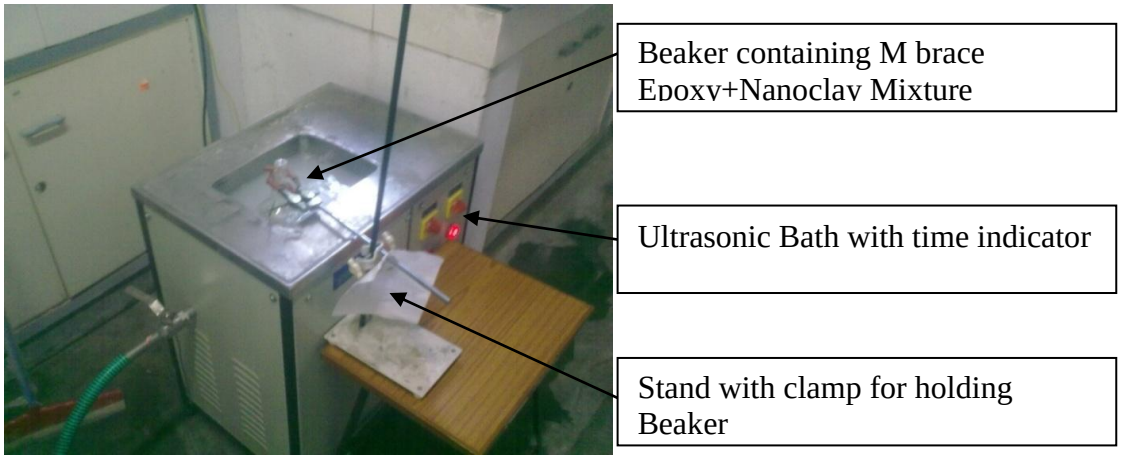


Fig.4.8: Ultrasonication bath

4.1.5 Mixing of epoxy base solution with hardener:

After ultrasonication, the solution is mixed with the hardener in the ratio 10:4 by volume. After mixing, mechanical stirring up to 5 to 10 minutes was done.

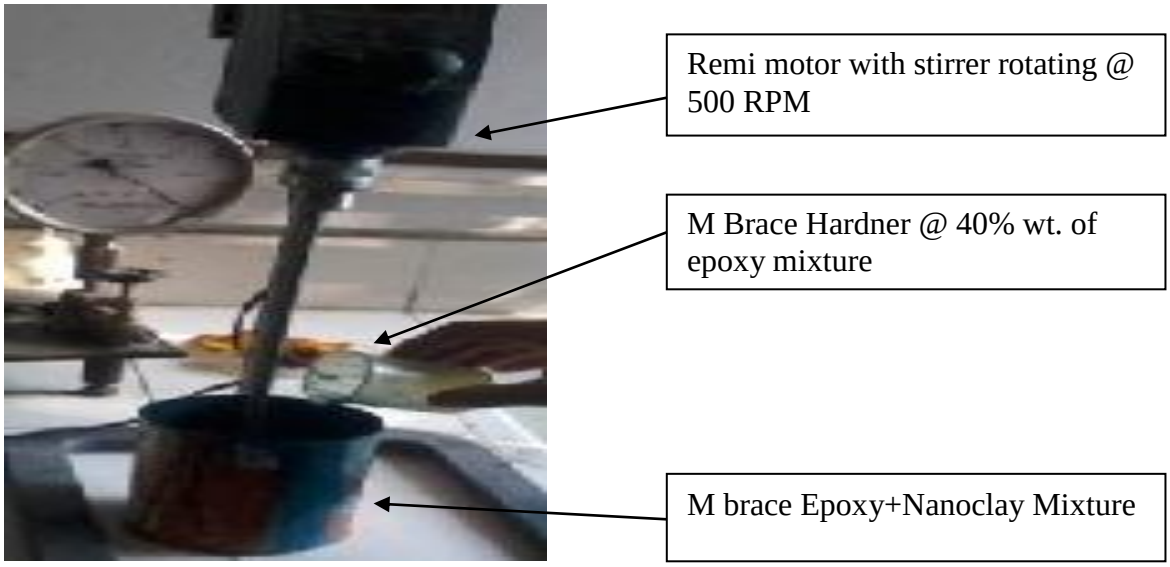


Fig 4.9 Mixing of epoxy base solution with hardener

4.1.6. Coating of nanoclay mixed epoxy to glass fiber sheets:

- (i) Making of 2% nanooclay-epoxy–Glass fiber Nano composite:

The mixture (Epoxy+2%Nano clay +Hardner) was poured on the glass fiber mat (E or C Glass Fiber) and applied uniformly using the hand layup method. For this, steel scraper was used to maintain uniformity of the solution. It was made sure that there is no air bubbles entrapped inside the epoxy applied on sheet otherwise it would create a flaw there. After applying epoxy on the both sides of first glass fiber, second fiber sheet was applied on first fiber sheet and epoxy was applied on second fiber sheet. Finally third fiber sheet was placed on second fiber sheet epoxy was applied on third fiber sheet.

- Making of 0% nanooclay-epoxy –Glass fiber Nano composite:

The same process (4.1.6.i) is repeated with use of Mixture of Epoxy+Hardner for making Base samples of EEE and CEC laminates.

As such following 04 types samples were prepared:

1. 0 % EEE Laminate.
2. 2% EEE Laminates

3. 0% CEC Laminates.
4. 2% CEC Laminates.

(a)

(b)

Fig. 4.10 (a & b) Coating the glass fiber sheet with epoxy solution

Fig. 4.11 Coated sheets placed for curing

4.1.7. Cutting of sheet for samples

The sheet took overnight to dry. The full curing of sheet (Fig. 4.7(a&b) & Fig. 4.8) was done by leaving it under ambient temperature for at least seven days before processing further. Once the epoxy was fully cured the samples were marked as per the ASTM dimensions for tensile & bending test and these marked samples were cut from the sheet to actual sample size using the marble cutter (Fig. 4.9).

Fig. 4.12 Marble cutter

4.1.8 Preparation samples for Thermal Aging and Moisture diffusion test.

Total 120 Nos of samples were cut from the Nano-composite sheets, the open four (Cutting) sides were applied with Mixture (Epoxy+hardner) and left it under ambient temperature for at least seven days for curing. The weight of each and every sample noted down before putting these samples for Hygrothermal testing. The marking was done on each and every sample to get track of sample after the test.

4.2. Experimental set-up for Thermal Aging and Moisture diffusion test.

A set of accelerated aging tests had been carried out to evaluate performance of glass fiber reinforced polymer (GFRP) sheets embedded in epoxy matrix (laminates). The field environment very similar to that of tropical climate had been simulated. The specimens were immersed in two

water baths for different time durations. Both of the water tanks were filled with water. One was of simple water and other tank was containing NaOH 5% by weight of water. Both the tanks were kept at a temperature of 45^{o}C.

The specimens were removed from the bath after an interval of 7 days, 15 days and 30 days. The samples were first dried with the help of tissue paper and the change in weight due to water ingress is noted down. The tensile and flexural strength was measured to check the degradation in properties of composite material. The SEM testing of broken samples during the tensile test was done to check the Fiber condition after 30 days water immersion test.

Fig. 4.13 Setup view of the water baths

4.2.1. Setup fabrication

Table 4.2 Shows that the set-up basically consists of following main items

Sl.No	Item No.	Quantity
1	Water Tank 60 Ltr Capacity	01 Nos.
2	Water+NaOH Tank 30 Ltr Capacity	01 Nos.
3	0% EEE Specimens	30 Nos
4	2% EEE Specimens	30 Nos.
5	0% CEC Specimens	30 Nos.
6	2% CEC Specimens	30 Nos.
	Total Specimens for testing	120 Nos.
7	Heating Elements	02 Nos.
8	RTD Sensors	02 Nos.
9	Temperature Controllers	02 Nos.

Table 4.2 Shows that the set-up basically consists of following main items

4.2.2. Water tanks

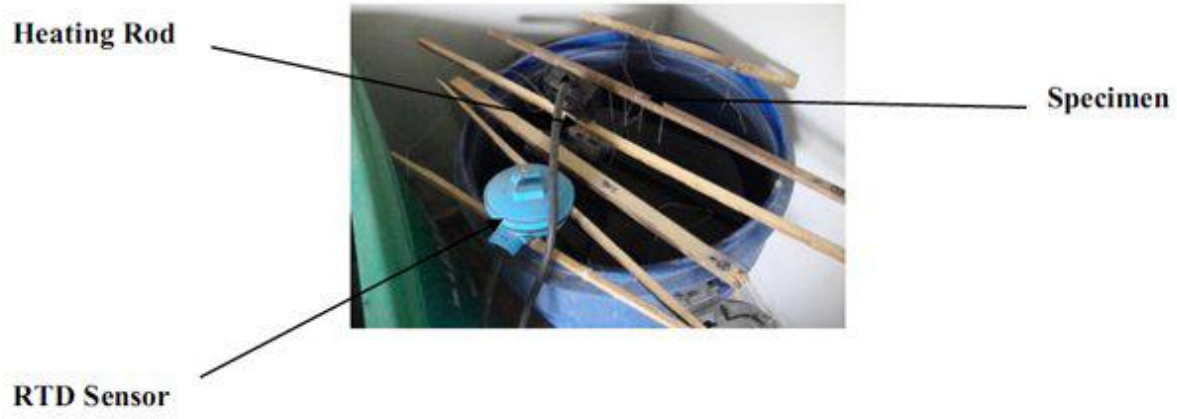
The experimental setup consists of two well insulated tanks (Fig. 4.10). The tank was of cylindrical shape and other of pyramid shape made out of plastic. The approximate capacity of the tank was 60 liters for water and 30 liter for Water+NaOh. Both the tanks were filled totally with tap water and set at a temperature of 45°C. NaOH was added to one tank (5% by weight of water). The water which evaporated from the tank was replenished on daily basis during experimentation. Each tank was labeled as per details of experimentation.

4.2.3. Heating element

The water/ Water+Naoh Tanks were heated with the help of commercially available heating rod elements (Fig. 4.11). Each bath was having its own heating rod connected via temperature controller (Fig.4.12). The wattage of rod was 1000KW with single phase connection. As the temperature reached the required value the power supply of rods were automatically cut off by controllers and also if temperature drops the required value the power supply of rods starts

automatically. This power on – power off process was controlled automatically with the help of sensors and controllers.

Fig. 4.14 Heating element and RTD sensor in a tank



4.2.5. Temperature controller

This set up was designed to maintain the bath temperature at 45^{o} till the duration (Max. duration was 30 days) of experiment for day and night on daily basis. So a temperature controller (Fig.4.12) was connected with each of the bath along with relays cut off. The controller used the proportional-integral-derivative (PID) control to maintain the temperature. On the controller display the "Set Value" was given which was the temperature indicated in green and the "Process Value" of temperature was indicated in the red (refer Fig.4.12), which was the output from the RTD sensor. For the very first time the controller was set to auto-tune mode so that it could adjust itself according to the input variables. Once the bath had attained the set value the controller cut off its supply and after sometime it sensed the temperature if it had gone below set value, it again started heating to obtain the set value. The dimensions of the controller and actual panel used are shown in Fig.4.12 and Fig. 4.13 respectively.

Fig. 4.15 (a) Temperature controller

Fig. 4.15 (b) Temperature display panel with controller

4.3. Testing methods used in experimentation

4.3.1 Moisture Detection and thermal Aging test

The specimens were removed from the bath after an interval of 7 days, 15 days and 30 days. The samples were first dried with the help of tissue paper and the change in weight due to water ingress is noted down. The weight of samples accurately checked using digital balance Make-Mettler Toledo , Model PB 303-S(Fig.4.14)

The relative mass change of the epoxy in the specimens under study expressed as a percentage was obtained using the expression:

$$\text{Increase in weight}\ (\%) = \frac{\text{weight}_{wet} - \text{weight}_{initial}}{\text{weight}_{initial}} \times 100$$

where Weight_{wet} is the weight of the epoxy matrix at a given immersion time, t, and $\text{Weight}_{initial}$, is the weight of the epoxy matrix at time, t = 0 for which the sample was considered dry

.

4.3.2. Tensile testing

A Universal tensile testing machine shown in Fig.4.15 and Fig.4.16 was used for the testing of the specimens for its tensile strength. The test specimen had been prepared according to ASTM

assumed dimensions. The specimen were tested until they break indicating the peak load and ultimate stress value they can bear at required time period to estimate the degradation in the same machine.

Fig. 4.16 UTM testing machine

Fig. 4.17 Specimen in jaws

4.3.3. Three point flexural test

Three point bending tests of specimen were carried out in using Zwick/Roell (Fig. 4.17 & Fig. 4.18).

Fig. 4.18 Three point bend test machine

Fig. 4.19 Specimen positioning

The test specimen had been prepared according to assumed dimensions. The three point bending test results can be taken as indications of strength degradation of composites after they had been hygrothermally treated.

4.3.4. Micro hardness test

Micro hardness test (shown in Fig.4.19) was conducted on specimen with different clay loadings and different Glass Fiber combination laminates to see the effect of clay loading and Glass Fiber combinations and on hardness values.

Fig. 4.20 Micro hardness equipment

Fig. 4.20 Indent of specimen

The load applied was 50gm and VHN values were determined by applying this load by using a calibration distance of 50 units in Quantinet software as shown in Fig.4.20 used for image analyzing. The dwell time used during load application was 20 seconds. An indent is formed in diamond shape used for calculating VHN as shown in figure below.

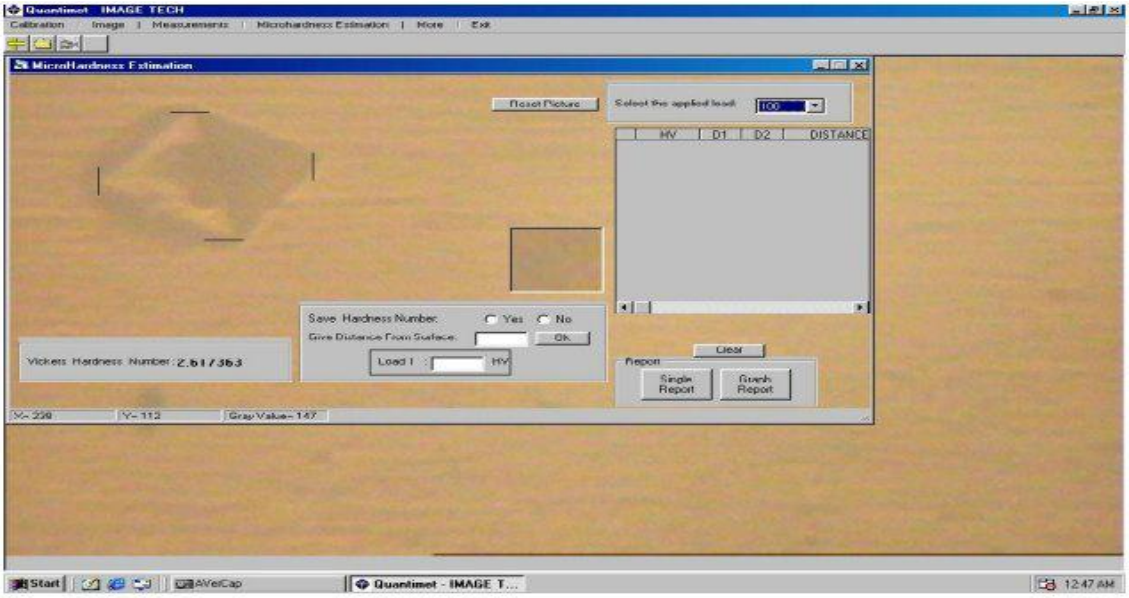


Fig. 4.21 Indent of specimen

4.3.5. X-Ray diffraction test

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

X-ray diffraction was used in this study to investigate the crystallographic structure of the epoxy Nano composites. XRD will enable the changes that occur to the clay due to the intercalation and/or exfoliation of the epoxy into the clay galleries to be quantified. The d-spacing of the intergallery spacing can be determined using Bragg‟s Law:

$\lambda = 2d\sin\theta$

Where λ is the wavelength of the incidence x-ray source, d is the spacing in question, θ is ½ of 2θ the Bragg angle or the diffracted angle of the incidence x-ray beam. Below is a schematic of the previously mentioned Bragg's Law (Fig. 4.22).

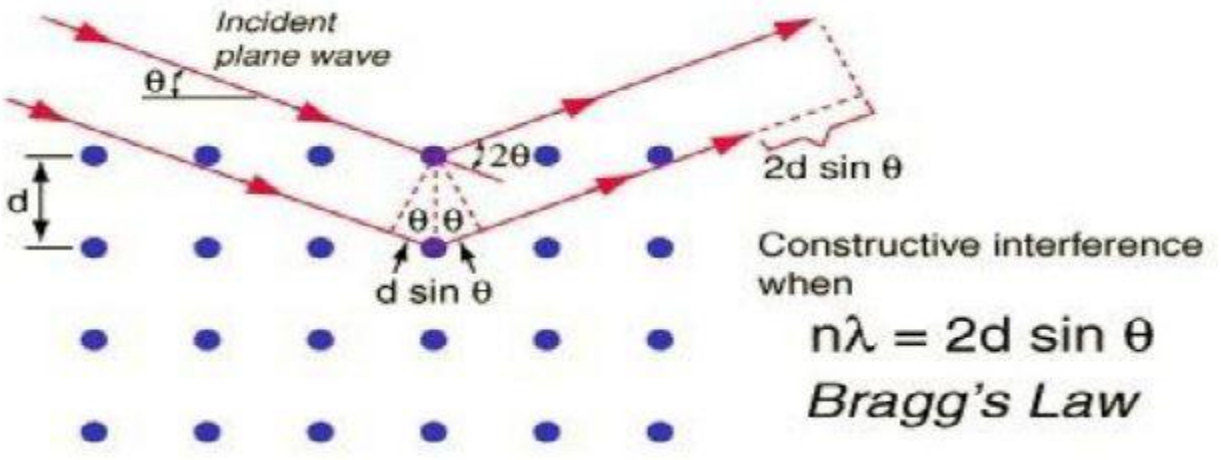


Fig. 4.22 Schematic representation of x-ray diffraction principle and the Bragg's Law

To evaluate the degree of exfoliation in the polymer, XRD measurements were carried out in a analytical X-ray diffractometer with Cu Kα radiation (λ=1.54Å) with a scanning speed of 10/min and at 45 kV and 40mA. During the XRD experiments, the samples were analyzed in reflection mode. All XRD scans were through 2θ of 5^{0} to 15^{0}.

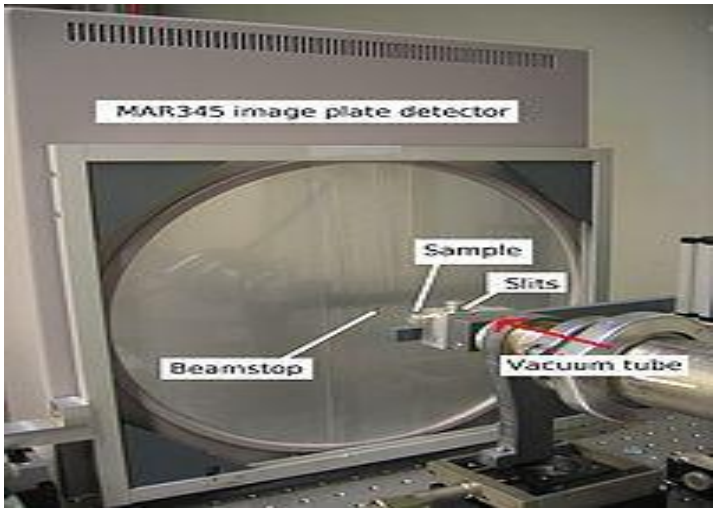


Fig.4.23 Schematic representation of x-ray Diffractometer principal

4.3.6 Scanning electronic microscope (SEM)

Scanning electronic microscope shown in Fig.4.23 was used to test Polymer fiber epoxy Nano composite specimen's microstructure. The dimensioning of specimen was done according to block size of machine. The polishing of specimen was done by using Gold coating equipment The polished specimen was used to observe the microstructure of specimen at different magnification

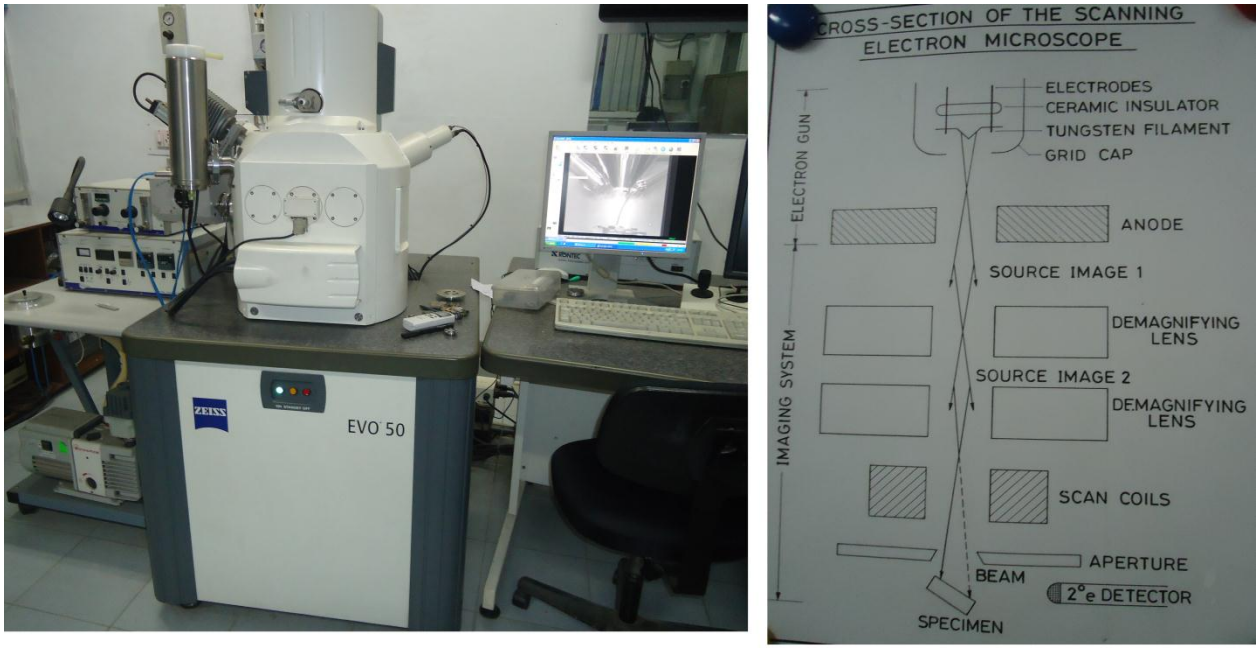


Fig 4.24 Scanning electronic microscope (SEM) Set up

SEM micrographs are helpful in viewing the micro-structure of material hence showing any changes in physical structure of material and showing any defects like cracks, voids generated after loading of clay and hygrothermal degradation of the material.

4.3.7. Transmission Electron Microscopy (TEM) is a vital characterization tool for directly imaging nanomaterials to obtain quantitative measures of particle and/or grain size and morphology.

TEM functions involve following basic operations:

A stream of electrons is formed and accelerated towards the specimen using a positive electrical potential, This stream is confined and focused using a metal aperture and magnetic lenses into a thin, monochromatic beam, (magnetic lenses are circular electro-magnets capable of projecting a precise circular magnetic field in a specified region, The focused beam is impinged on the sample by a magnetic lens, The energetic electrons then interact with the irradiated sample. These interactions and effects are detected and transformed into an image.

We use a HITACHI transmission electron microscope operating at an accelerating voltage of 80KV is used in this study to test the morphology and particle size. Sample in powder form is prepared for imaging by drying nanoparticles on a copper grid that is coated with a thin layer of carbon.

4.4 Test matrices Table 4.3 shows no of specimens prepared for different test.

Specimen Name		No. of Specimen				Total Specimen
		Tensile	Micro Hardness	Bending	SEM	
0% EEE	0 day water test	3	1	3	1	8
	7 day water test	3	-	3	-	6
	15 day water test	3	-	3	-	6
	30 day water test	3	-	3	-	6
	15 day NaoH+water	3	-	3	-	6
2% EEE	0 day water test	3	1	3	1	8
	7 day water test	3	-	3	-	6
	15 day water test	3	-	3	-	6
	30 day water test	3	-	3	1	7
	15 day NaoH+water	3	-	3	-	6
0% CEC	0 day water test	3	1	3	1	8
	7 day water test	3	-	3	-	6
	15 day water test	3	-	3	-	6
	30 day water test	3	-	3	-	6
	15 day NaoH+water	3	-	3	-	6
2% CEC	0 day water test	3	1	3	1	8
	7 day water test	3	-	3	-	6
	15 day water test	3	-	3	-	6
	30 day water test	3	-	3	-	6
	15 day NaoH+water	3	-	3	1	7
Total Specimens						130

Table 4.3 Test matrices

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Water Absorption and Diffusivity test:

5.1.1 Water absorption studies:

Water ingress in samples subjected to exposure of hot water condition and hot NaOH+water condition for the period of 7 days, 15 days and 30 days is measured and compared with the initial weight of these samples. The table 5.1 & 5.2 presents the summary of weight of samples before immersion and after immersion for the period of 7 day, 15 day & 30 day in hot water and hot NaOh-water for four type of samples. The percentage relative weight gain (Wt) is calculated using the formula mentioned at 4.4.1 and average weight gain for the specific period is calculated of each Nano composite laminate system.

Table 5.1:Hygrothermal Test results for EEE laminates

Sample No.	0 % EEE				2% EEE			
7 day's Immersion in water	Weight Initial	Weight Wet	% Weight increase (Wt)	% Average Weight increase	Weight Initial	Weight Wet	% Weight increase (Wt)	% Average Weight increase
1st	13.305	13.652	2.542		12.082	12.354	2.202	
2nd	13.442	13.815	2.700		11.372	11.615	2.092	
3rd	10.092	10.392	2.887		12.363	12.631	2.122	
4th	13.218	13.525	2.270	2.71	12.532	12.827	2.300	2.16
5th	13.172	13.612	3.232		12.436	12.689	1.994	
6th	11.796	12.12	2.673		13.821	14.143	2.277	
15 days								
1st	15.495	16.165	4.145		10.858	11.389	4.662	
2nd	13.732	14.453	4.989		14.454	14.968	3.434	
3rd	12.514	13.14	4.764		13.311	13.815	3.648	
4th	14.573	15.276	4.602	4.68	13.034	13.546	3.780	3.77
5th	14.188	14.905	4.810		15.026	15.552	3.382	
6th	13.215	13.879	4.784		13.82	14.352	3.707	
30 days								
1st	14.101	14.875	5.203		10.858	11.257	3.544	
2nd	12.961	13.582	4.572		14.454	14.968	3.434	
3rd	14.186	14.912	4.869		13.311	13.815	3.648	
4th	14.153	14.897	4.994	4.73	13.034	13.546	3.780	3.88

5th	12.031	12.684	5.148		15.026	15.552	3.382	
6th	12.345	12.785	3.442		13.82	14.301	3.363	

Naoh for 15 days

1st	13.829	14.356	3.671		12.788	13.362	4.296	
2nd	13.387	13.985	4.276		14.399	14.985	3.911	
3rd	12.944	13.634	5.061		13.648	14.064	2.958	
4th	14.251	15.105	5.654	4.70	13.057	13.548	3.624	3.78
5th	12.272	12.952	5.250		14.059	14.556	3.414	
6th	13.387	13.984	4.269		12.171	12.756	4.586	

Table 5.2 Hygrothermal Test results for CEC laminates

	0 % CEC				2% CEC			
7 day's Immersion in water	Weight Initial	Weight Wet	% Weight increase (Wt)	% Average Weight increase	Weight Initial	Weight Wet	% Weight increase (Wt)	% Average Weight increase
1st	11.685	11.895	1.765		13.326	13.568	1.784	
2nd	10.938	11.148	1.884		14.202	14.384	1.265	
3rd	12.451	12.659	1.643		13.455	13.621	1.219	
4th	11.191	11.358	1.470	1.69	13.184	13.375	1.428	1.40
5th	12.668	12.874	1.600		13.984	14.176	1.354	
6th	11.201	11.406	1.797		14.155	14.354	1.386	

15 days

1st	11.685	12.085	3.310		11.763	12.054	2.414	
2nd	11.993	12.358	2.954		12.482	12.784	2.362	
3rd	11.584	11.925	2.860		10.222	10.456	2.238	
4th	11.657	12.025	3.060	2.822	11.921	12.254	2.717	2.66
5th	11.155	11.375	1.934		11.705	12.056	2.911	
6th	12.743	13.112	2.814		11.199	11.584	3.324	

30 days

1st	14.12	14.568	3.075		12.635	12.969	2.575	
2nd	11.584	11.965	3.184		13.695	14.085	2.769	
3rd	11.657	12.048	3.245		13.312	13.645	2.440	
4th	14.425	15.029	4.019	3.09	13.439	13.874	3.135	2.707
5th	11.368	11.746	3.218		12.41	12.723	2.460	
6th	11.315	11.523	1.805		12.888	13.268	2.864	

Naoh for 15 days

1st	16.015	16.457	2.686		12.48	12.845	2.842	
2nd	13.597	13.985	2.774		11.683	11.987	2.536	
3rd	15.204	15.448	1.579		11.385	11.765	3.230	
4th	13.497	13.847	2.528	2.81	13.705	14.097	2.781	2.68
5th	15.472	16.08	3.781		12.98	13.258	2.097	
6th	16.342	16.954	3.610		12.737	13.08	2.622	

From the above mentioned Tables (5.1 and 5.2) it was observed that the water diffusivity decreases with the addition of Nano clay. It decreases by 24 to 27% as compared to neat epoxy laminates. It is also revealed that water diffusivity mostly affected by the nature of glass fiber used. Water absorbed by CEC glass fiber laminate is very less and water diffusivity was decreased by 55% to the corresponding EEE glass fiber laminates.

Water Uptake as a function of duration of exposure is presented in fig 5.1,5.2 ,5.3 & 5.4 and comparative graph of these four types of samples for average weight gain Vs days of exposure is presented in Fig.5.5 and comparative graph of percentage average weight gain for four type of samples for different atmospheric/tropical conditions is presented in Fig 5.6

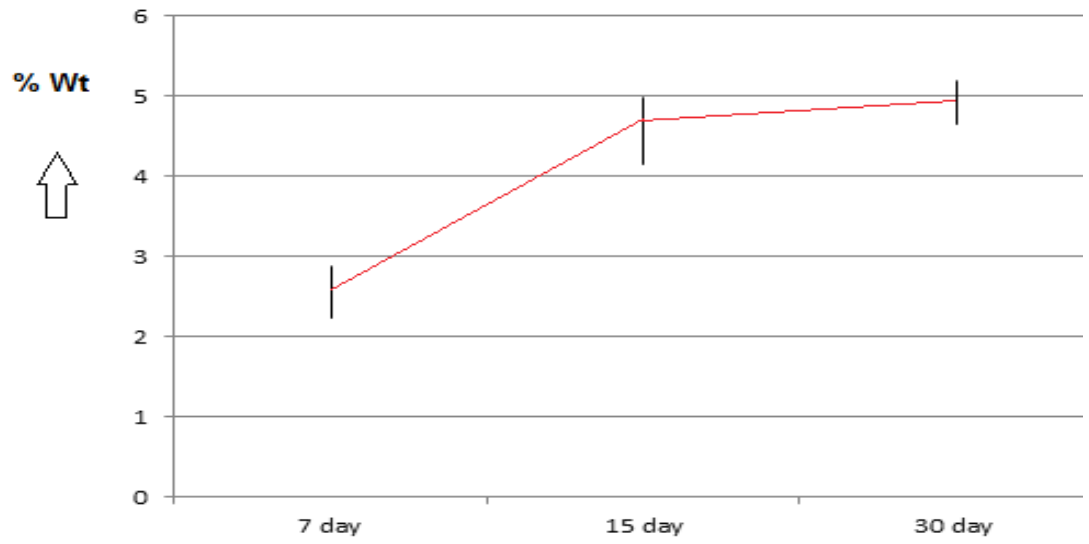


Fig 5.1 Relative percentage Weight gain to the days of exposure for 0% EEE Specimens

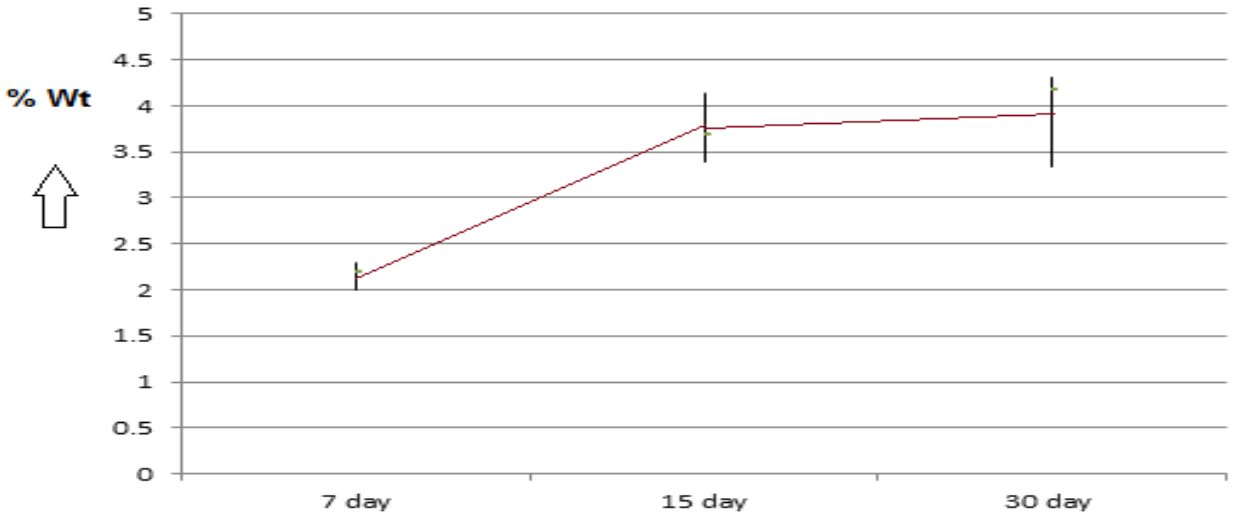


Fig 5.2 Relative percentage Weight gain to the days of exposure for 2% EEE Specimens

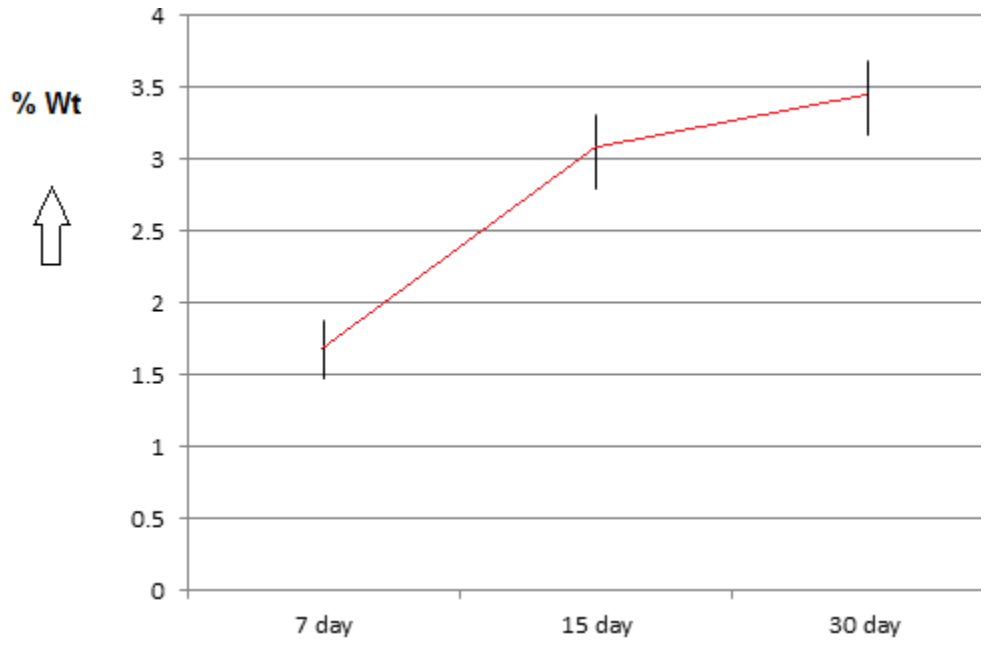


Fig 5.3 Relative percentage Weight gain to the days of exposure for 0 % CEC Specimens

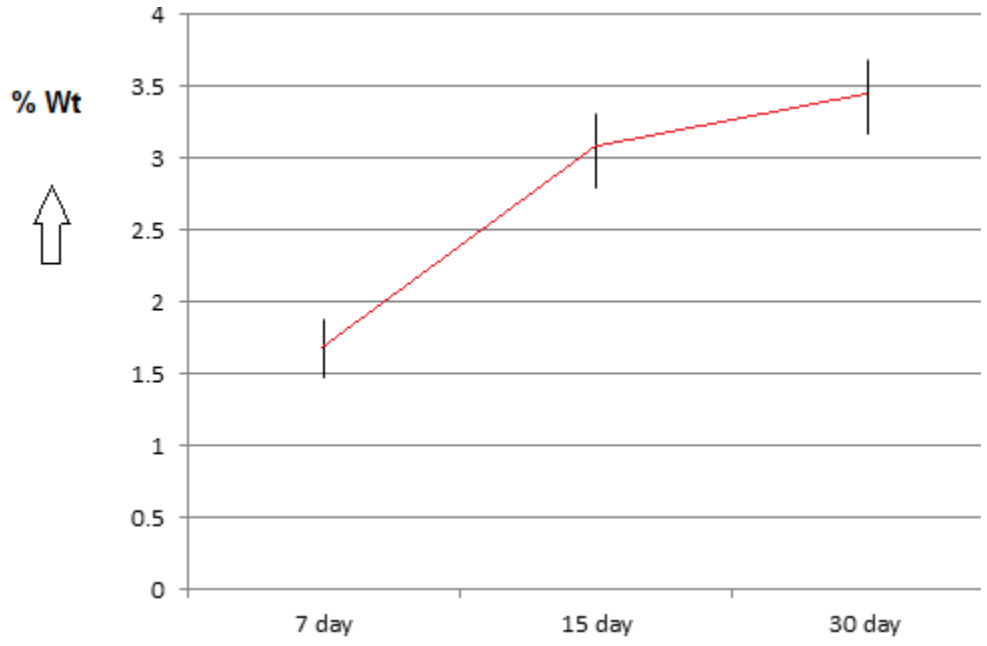


Fig 5.4 Relative percentage Weight gain to the days of exposure for 0 % CEC Specimens

From the above mentioned graphs (5.1, 5.2, 5.3 & 5.4), it is observed that water absorption increases with increase in immersion time of all samples. Water uptake is linear and very rapid in the beginning of the exposure after which it slows down and reaches saturation level.

Graphs 5.5 shows comparative trend of average weight gain over different intervals for the four type of systems. It is observed that 0% EEE Nano-composite is having maximum average weight gain in comparison to all other Nano-composites , whereas 2% CEC Nano composite is having lowest average weight gain under the similar conditions.

Graph 5.6 shows that percentage average weight gain over different intervals for the four Nano composites under two different tropical conditions. It is observed that the Nano composites subjected to NaOH+water hot wet environment get maximum water uptake during the 15 days of period. The water uptake under these condition is nearly at par with saturation level. Thus the nano composites have tendency to absorb more water in NaOH+water hot environment as compared to hot water environment.

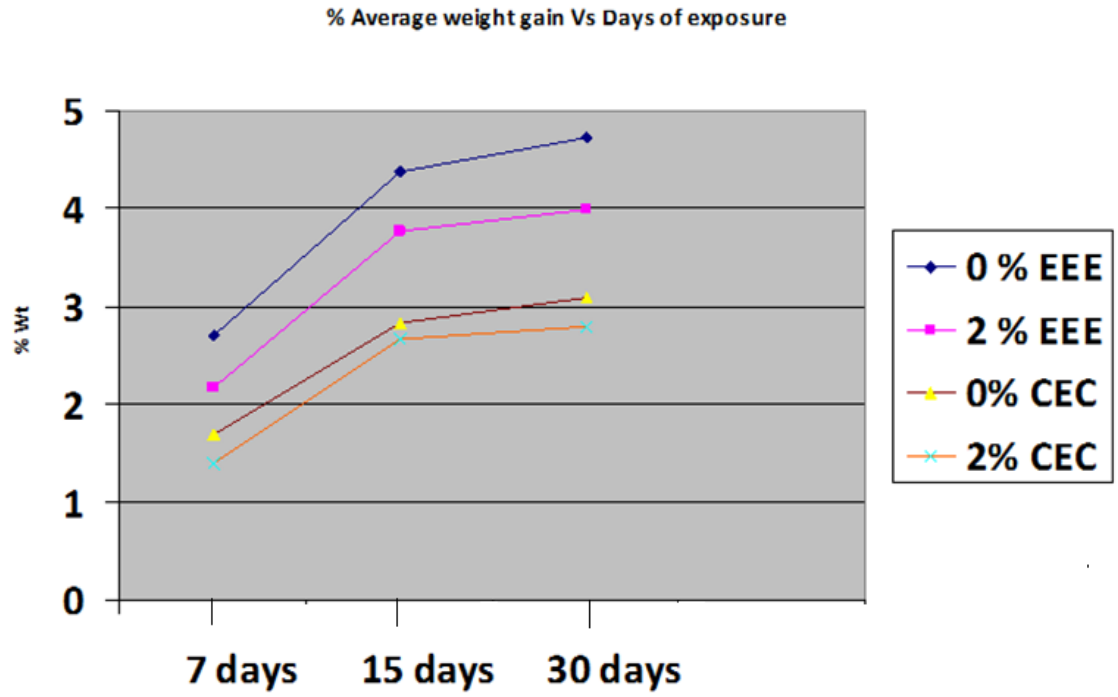


Fig 5.5 % Average Wt gain Vs days of exposure for 4 types of specimens.

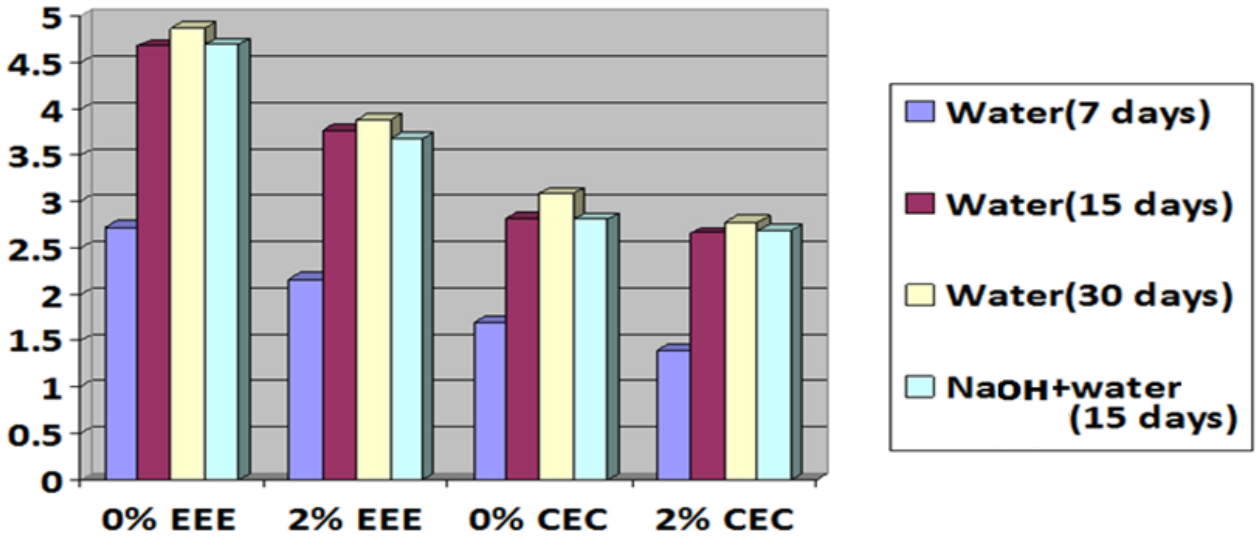


Fig 5.6 Average Wt gain Vs conditions of exposure for 4 types of specimens.

5.1.2 Diffusion Studies

The Fick's second law of diffusion can be used to study the diffusion mechanism in polymer composites. The diffusion coefficient D can be computed using the formula as per Gopalan et al. [5]:

$$D = \pi \left(\frac{h}{4M_{\infty}} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{(t_2 - t_1)}} \right)^2$$

where, M_1 and M_2 are the water contents at time $t_1$and t_2, respectively, h is the thickness of the specimen in mm and M_∞ is the maximum water uptake.

Sl.No	Nanocomposite	Max. % Water uptake	Diffusion coefficient (m^2/s)
1	0% EEE	4.73	1.70×10^{-12}
2	2% EEE	3.88	1.78×10^{-12}
3	0% CEC	3.09	1.98×10^{-12}
4	2% CEC	2.77	2.13×10^{-12}

Table 5.3 Maximum Water uptake and diffusion coefficient for different nano-composites

Table 5.3 shows that velocity of water ingress into the epoxy Nano composite follows the order 0% EEE > 2% EEE > 0% CEC > 2% CEC from the column of Max % Water uptake. Amount of water absorbed decreases follows the order 2% CEC > 0%CEC >2% EEE> 0% EEE seen from the column of diffusion coefficient. It shows that water uptake in epoxy Nano composite system depends on presence and nature of Glass fiber. The presence of Nano clay also plays some effect and it also reduces water ingress which indicates lower diffusion coefficient for 2% EEE as compared to 0% EEE because of 2% Nano clay and low diffusion coefficient for 0%CEC as compared to 0% EEE and 2% EEE because of use of C Glass fiber and very low diffusion coefficient for 2% CEC as compared other three Nano composite systems.

5.2 MICROSCOPIC BEHAVIOR

5.2.1 Micro-Hardness

5.2.1.1 Specimen for micro hardness

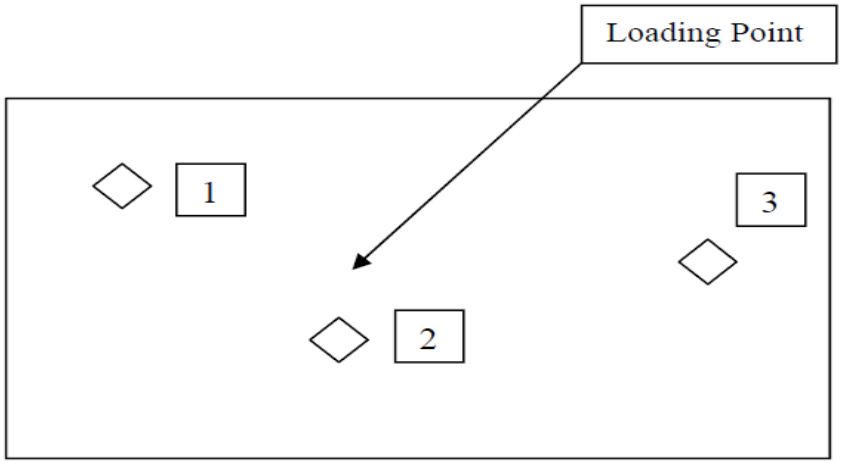


Fig. 5.7 Location of loading points in specimen

The micro-hardness of specimen manufactured at different clay loading was measured. The table 5.4 show the experimental observations of the Nano composites with different Nano clay contents and with different epoxy Nano composites. An average hardness was calculated by taking measurements at 3 points in each specimen. Fig 5.7 shows the results of Vickers hardness plotted against Nano clay loading.

Clay loading / Loading Points	Micro hardness values			
	0% EEE	2 % EEE	0% CEC	2% CEC
1st Indent	6.127412	7.281214	6. 412129	8.167143
2nd Indent	6.640959	8. 143167	5.682314	7.281412
3rd Indent	5.614823	7.157596	6.610951	7.159576
Average	6.127731	7.527325	6.235131	7.535604

Table 5.4 Micro hardness values for different clay loading specimens Clay Loading

The maximum hardness has been measured where the Nano clay content reached 2 wt%. The nature of fiber does not affect the hardness of the Nano composites. For both the Nano composites the hardness pattern is similar for 0% EEE and 0% CEC and also it is similar for 2 % EEE and 2 % CEC. Thus the hardness of the Nano composite is dependent on the percentage of Nano clay content and not dependent on the type and nature of glass fiber.

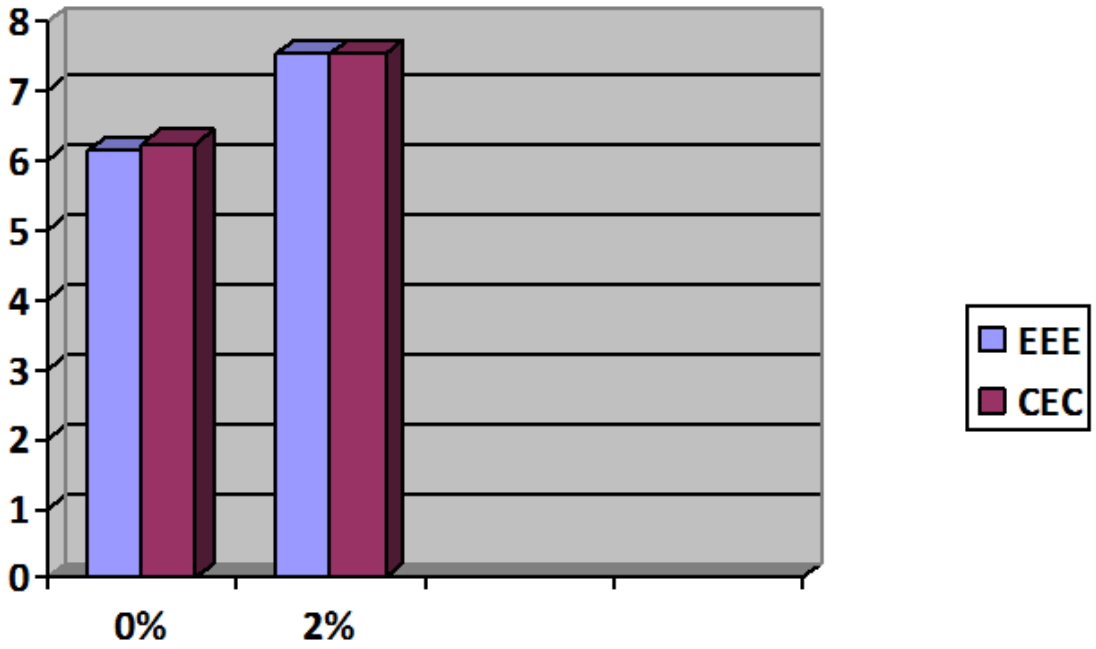


Fig. 5.8 The Vickers' hardness value of specimen as a function of weight percentage of Nano clay in epoxy for two Nano composite systems

5.2.2 X-ray diffraction test

The X-ray Diffraction experiments were conducted on the specimen having 2% Nano clay loading. X-ray diffractometer gives the values of d-spacing and 2θ for this specimen of epoxy clay Nano composite. An increase of the interlayer distance leads to a shift of the diffraction peak toward lower angle. The diffraction peak of Closite 30B comes out at an angle 2θ = 4.8452 and corresponding d-spacing value is d = 18.26854.

S.No.	Clay Loading	Angle(2θ)	d- Spacing
1	Closite 30B	4.8452	18.26854
2	2 wt.%	Exfoliation	------

Table 5.5: d- Spacing of Clay & Epoxy layered silicates

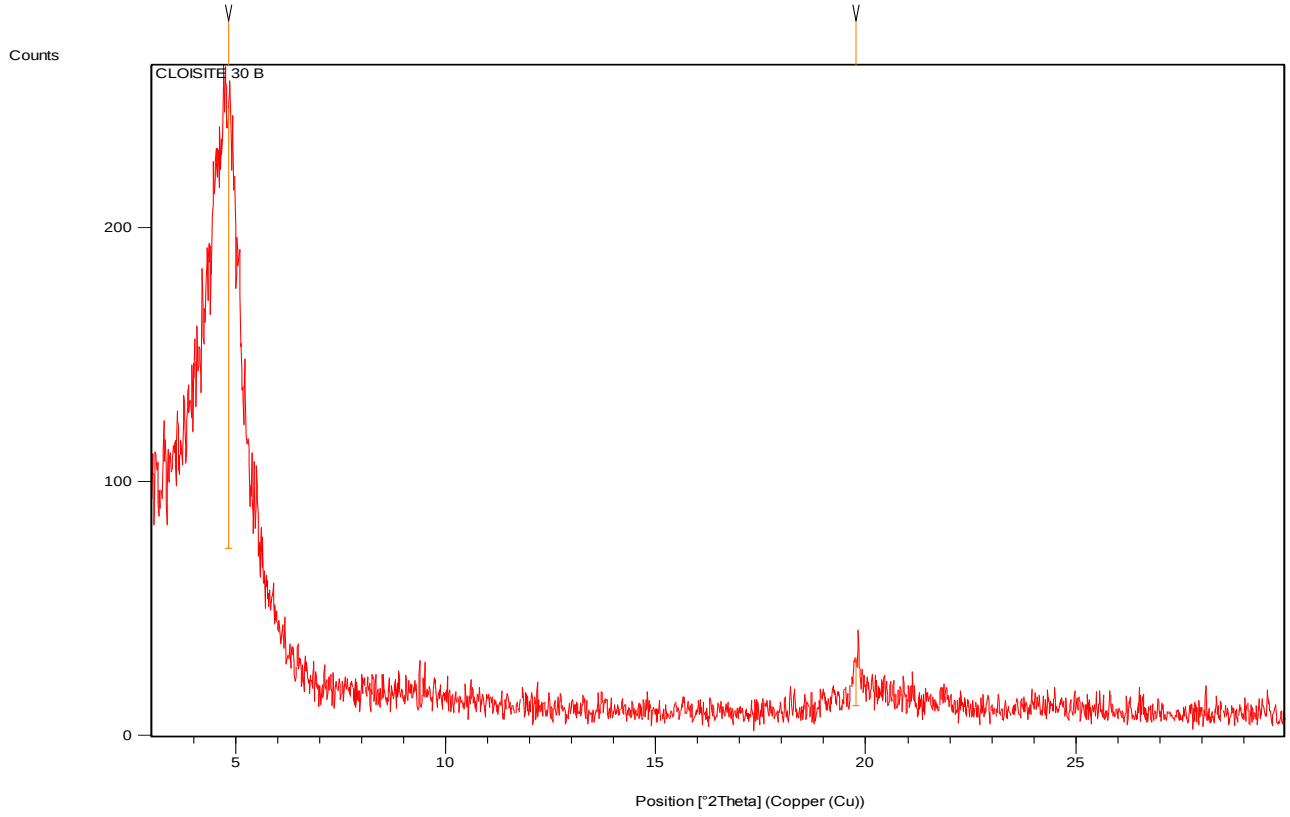


Fig. 5.9 a XRD result Nanoclay clay

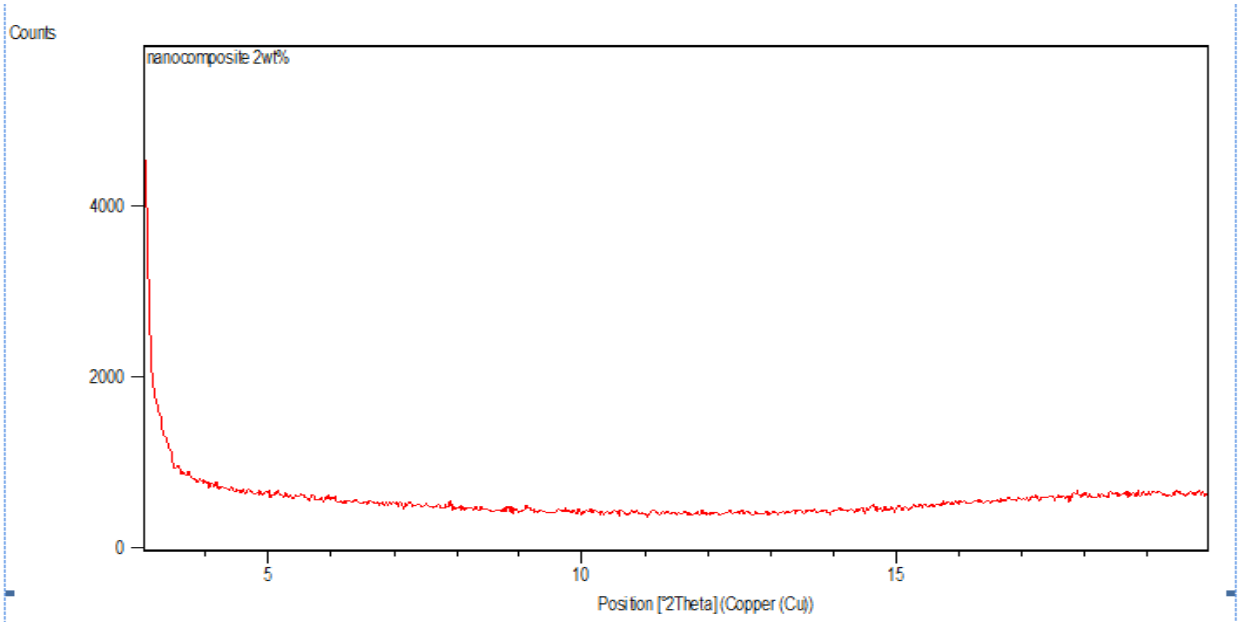


Fig. 5.9 b XRD result of specimen with 2% clay

The absence of peaks in diffraction pattern indicated formation of exfoliated Nano composites at the level of Nano clay loading.

5.2.3 Transmission electron microscopy (TEM):

Fig 5.10, 5.11 and 5.12 shows the morphology of Nano composites containing 2wt% clay loadings in Transmission electron microscopy (TEM) test. In this test , Sample in powder form was dissolved in ethanol and sonicated for 1hour prior to dispersion onto a copper grid using a porous carbon film. The morphological detail of the sample was determined at various magnifications TEM images, The image shows a very uniform distribution of Nano clay particles. The particles appear to be agglomeration-free and the individual particles can be identified very clearly. It shows exfoliated structure and the clay platelets of nanometer thickness dispersed in the polymer matrix are clearly visible.

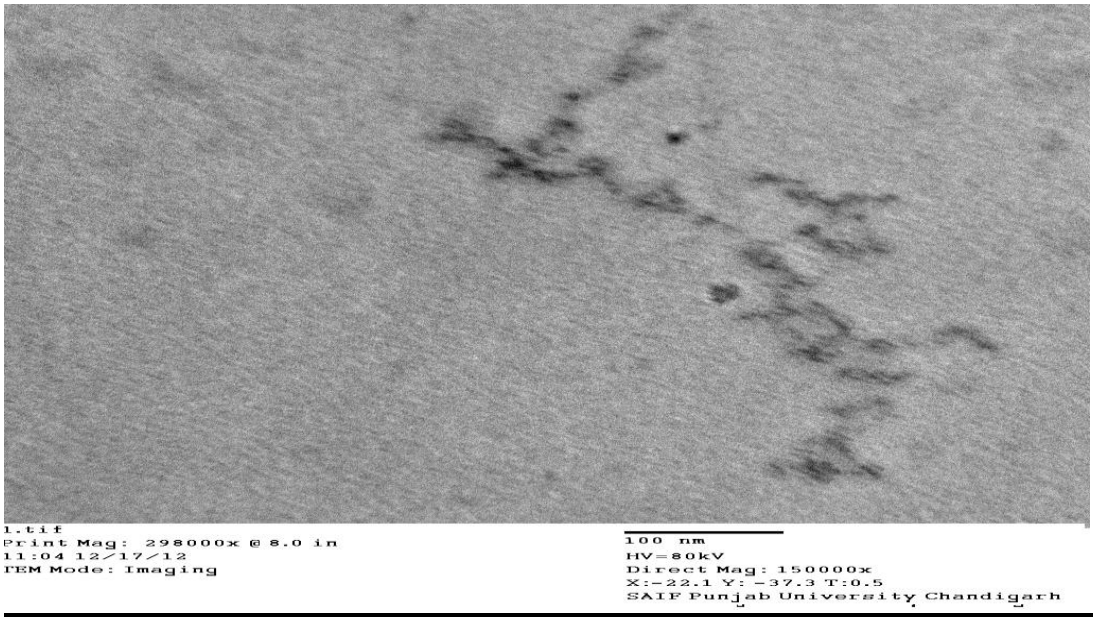


Fig. 5.10 TEM micrograph of 2 wt% Nano clay at 150000 X

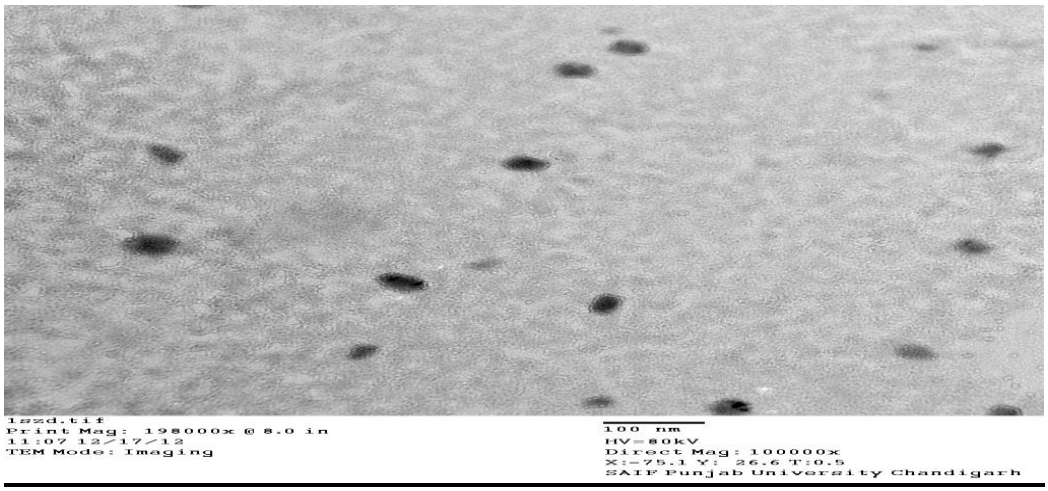


Fig. 5.11 TEM micrograph of 2 wt% Nano clay at 100000 X

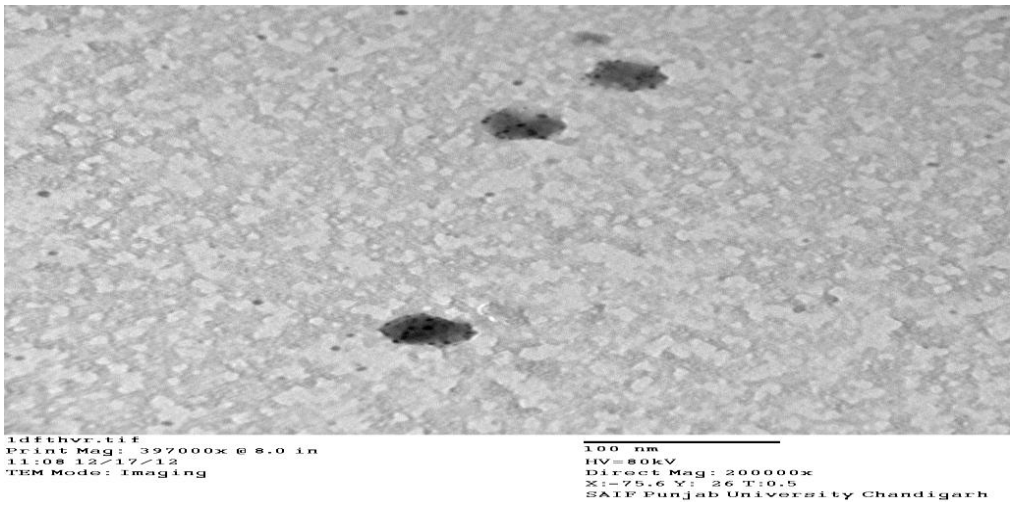


Fig. 5.12 TEM micrograph of 2 wt% Nano clay at 200000 X

5.2.4 Scanning Electron Microscopy(SEM): Fig 5.13 to 5.18 illustrates the SEM fracture surface images of glass fabric reinforced laminates obtained from tensile test specimens prepared with epoxy,nanoclay and glass fibre laminates respectively.

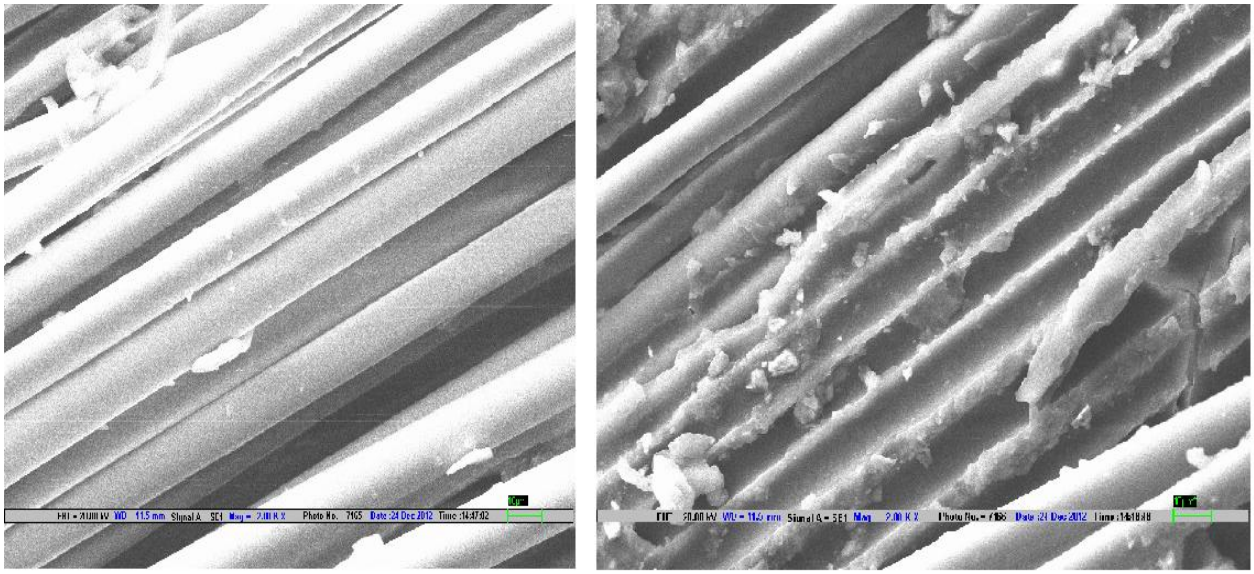


Fig 5.13 SEM micrographs of the tensile fractured 2% EEE specimens

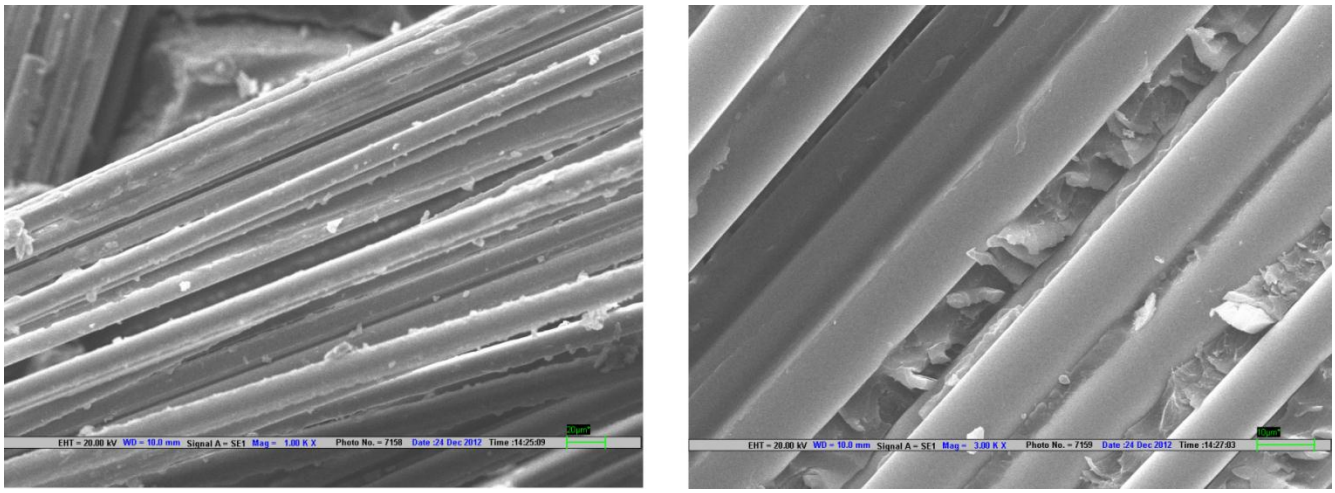


Fig 5.14 SEM micrographs of the tensile fractured 2% EEE specimens subjected to 30 days exposure to hot water @ 45^{o} temp.

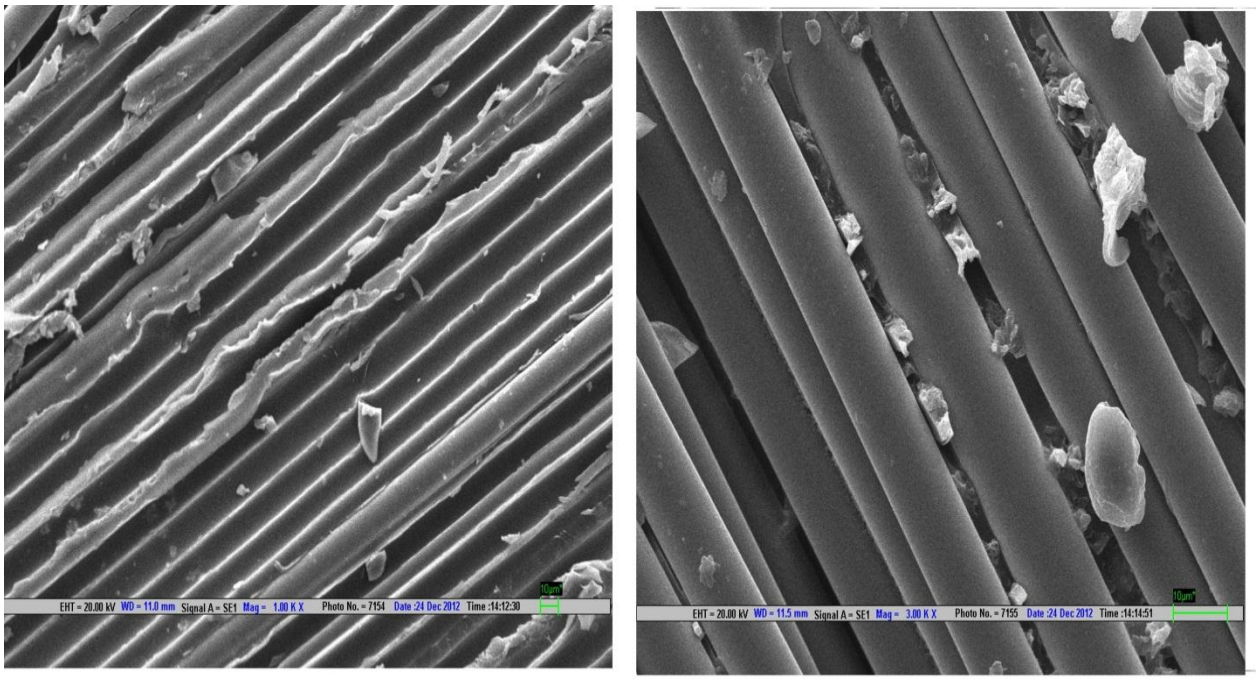


Fig 5.15 SEM micrographs of the tensile fractured 2% CEC specimens subjected to 30 days exposure to hot water @ 45^{o} temp.

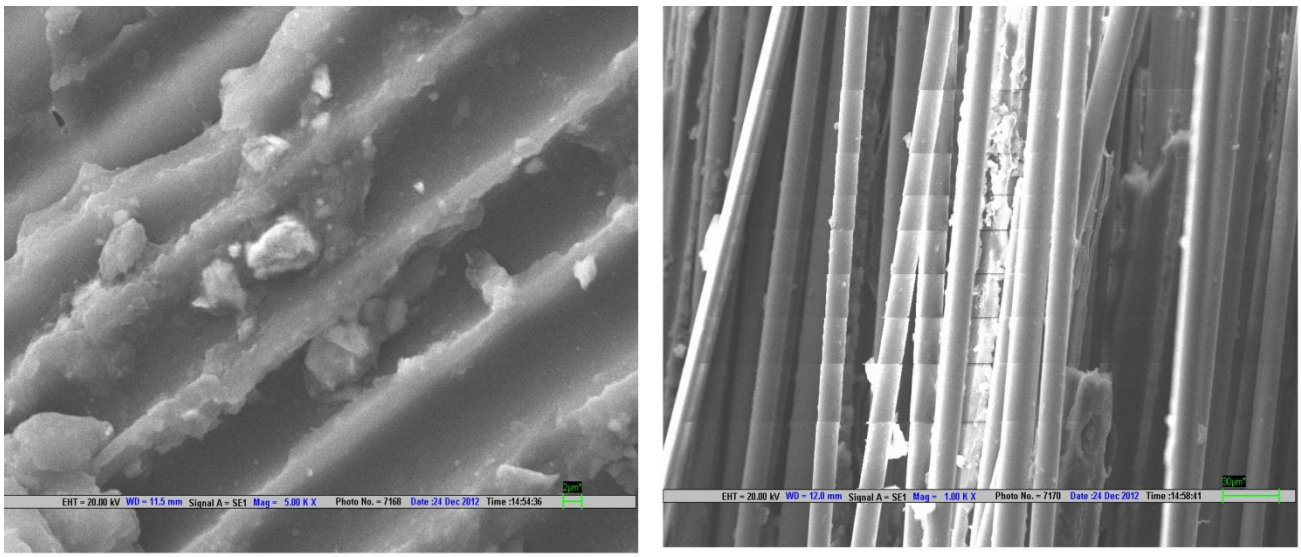


Fig 5.16 SEM micrographs of the tensile fractured 2% EEE specimens subjected to 15 days exposure to hot NaOH+water solution @ 45^{o} temp.

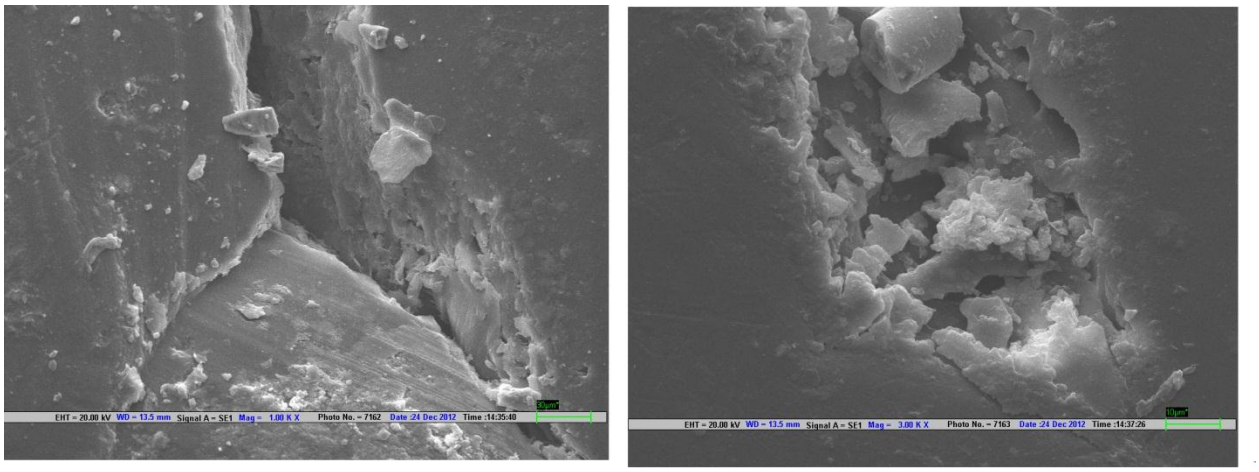


Fig 5.17 SEM micrographs of the degradation of 2% EEE specimens subjected to 15 days exposure to hot NaOH+water solution @ 45^{o} temp.

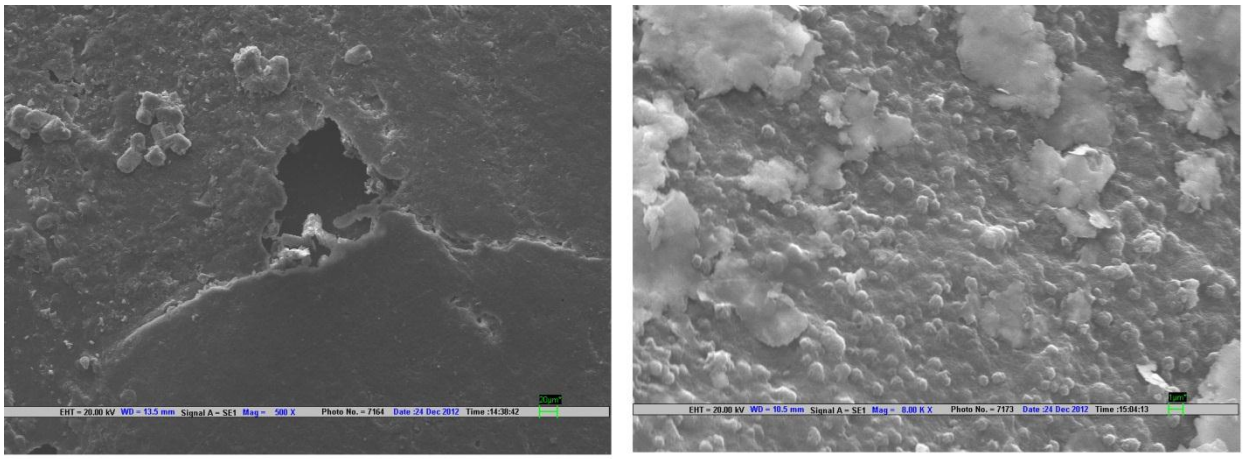


Fig 5.18 SEM micrographs of the degradation of 2% CEC specimens subjected to 15 days exposure to hot NaOH+water solution @ 45^{o} temp.

SEM analysis provides evidence of the resin/fibre binding in fractured specimens. The degradation in mechanical properties is due to the degradation in fibre/matrix interface bonding. The voids present in the matrix are the main reasons for moisture diffusion. The microcracks formed during the composite preparation or by the service condition can store the trapped water. The voids and microcracks in the specimens can be traced using SEM images. Figures 5.13 to 5.16 show the micrographs of the tensile fractured specimens. Fig 5.16 shows the degradation of Glass fibre and cracking / breaking in glass fibre due to exposure to hot NaOH+water solution. The glass fibre weakens due to water+NaOH ingress. This indicates that the failure in Nano composites was due to combined effect of matrix cracking, delamination and fibre breakage.

Fig 5.17 and 5.18 shows the degradation of epoxy surface and cracking of glass fibre at outer layer due to exposure of Nano composite to NaOh+water hot environment. This clearly shows the maximum degradation occurs for EEE neat system than other system, addition of Nano clay reduces degradation as well as fibre breakage. CEC Nano composite offers maximum resistance to degradation, it is due to C Glass fibres ability to resist corrosion under the hot wet conditions.

5.3 Tensile test

The results obtained by conducting tensile tests on Nano composites using Zwick/Roell universal testing machine are shown in table 5.6 & 5.7

No. of Days	Sample Name	Sample No. Tensile	Modulus (MPa)	Tensile Strength(MPa)	% Decrease in strength
0 Day	0 % EEE	sample No 1	7150	82.74	
		sample No 2	6620	84.46	
		sample No 3	4680	79.98	
		Average		82.39	
	2% EEE	sample No 1	4430	79.27	
		sample No 2	3500	88.25	
		sample No 3	3410	84.95	
		Average		84.16	
	0 % CEC	sample No 1	3680	81.5	
		sample No 2	5060	76.45	
		sample No 3		87.34	
		Average		81.76	
	2% CEC	sample No 1	2320	82.6	
		sample No 2	1880	90.1	
		sample No 3	2456	89.35	
		Average		87.35	
7 Day	0 % EEE	sample No 1	7150	84.85	
		sample No 2	6620	81.57	
		sample No 3	7254	76.49	
		Average		80.97	1.72
	2% EEE	sample No 1	4430	79.34	
		sample No 2	3500	81.25	
		sample No 3	3754	87.75	
		Average		82.78	1.63
	0 % CEC	sample No 1	3680	77.38	
		sample No 2	5060	74.69	
		sample No 3	4685	88.71	
		Average		80.26	1.85
	2% CEC	sample No 1	2320	73.34	
		sample No 2	1880	75.11	
		sample No 3	2487	77.45	
		Average		75.3	1.38

15 Day	0 % EEE	sample No 1	7150	77.86	
		sample No 2	6620	81.24	
		sample No 3	5460	82.28	
		Average		80.46	2.34
	2% EEE	sample No 1	4430	78.76	
		sample No 2	3500	80.58	
		sample No 3	4278	87.83	
		Average		82.39	2.11
	0 % CEC	sample No 1	3680	74.14	
		sample No 2	5060	82.47	
		sample No 3	4850	82.91	
		Average		79.84	2.35
	2% CEC	sample No 1	2320	87.82	
		sample No 2	1880	84.97	
		sample No 3	2458	81.79	
		Average		85.98	1.57
30 Day	0 % EEE	sample No 1	1920	87.29	
		sample No 2	1870	75.36	
		sample No 3	1684	77.47	
		Average		80.04	2.91
	2% EEE	sample No 1	1320	84.46	
		sample No 2	1330	78.48	
		sample No 3	1480	82.64	
		Average		81.86	2.69
	0 % CEC	sample No 1	3680	65.47	
		sample No 2	5060	87.96	
		sample No 3	4876	83.12	
		Average		78.85	3.547
	2% CEC	sample No 1	2320	91.57	
		sample No 2	1880	73.18	
		sample No 3	2154	88.57	
		Average		85.77	1.81

Table 5.6 Results of specimens subjected to hygrothermal test in water @ 45^{o} temp over different days of exposure from tensile test.

0 Day	0 % EEE	sample No 1	7150	82.74	
		sample No 2	6620	84.46	
		sample No 3	4680	79.98	
		Average		82.39	
	2% EEE	sample No 1	4430	79.27	
		sample No 2	3500	88.25	
		sample No 3	3410	84.95	
		Average		84.16	
	0 % CEC	sample No 1	3680	81.5	
		sample No 2	5060	76.45	
		sample No 3		87.34	
		Average		81.76	
	2% CEC	sample No 1	2320	82.6	
		sample No 2	1880	90.1	
		sample No 3	2456	89.35	
		Average		87.35	
15 Day NaOH	0 % EEE	sample No 1	7150	31.59	
		sample No 2	6620	24.68	
		sample No 3	4680	25.48	
		Average		27.25	66.92
	2% EEE	sample No 1	1130	30.55	
		sample No 2	895	26.84	
		sample No 3	941	24.35	
		Average		29.58	68.42
	0 % CEC	sample No 1	3680	40.64	
		sample No 2	5060	39.74	
		sample No 3		42.62	
		Average		41.25	49.14
	2% CEC	sample No 1	2320	54.78	
		sample No 2	1880	60.98	
		sample No 3	2456	56.15	
		Average		57.31	34.44

Table 5.7 Results of specimens subjected to hygrothermal test in NaOH+water @ 45^{o} temp over different days of exposure from tensile test.

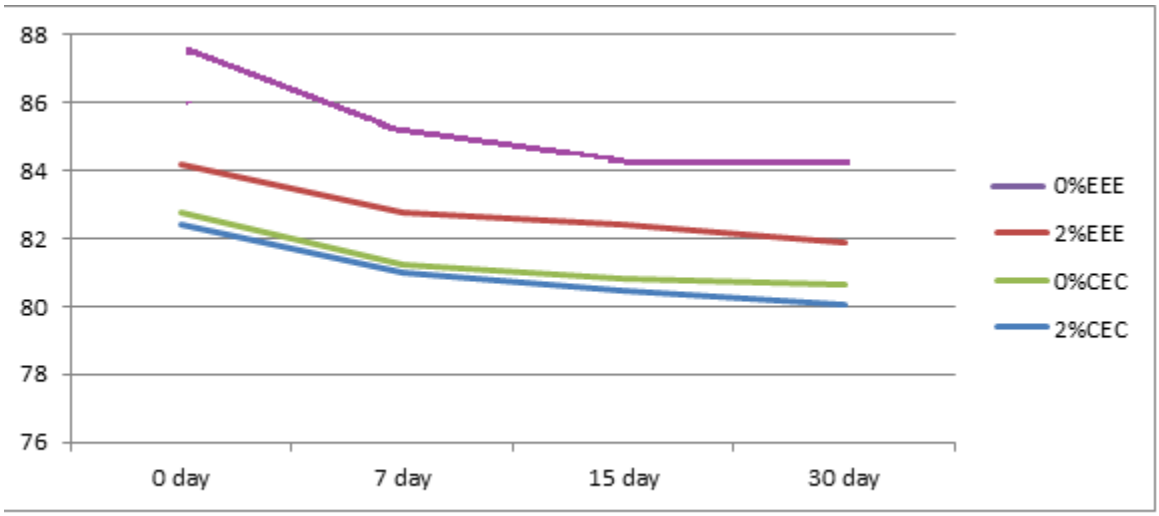


Fig 5.19 Decrease in tensile strength after degradation in water

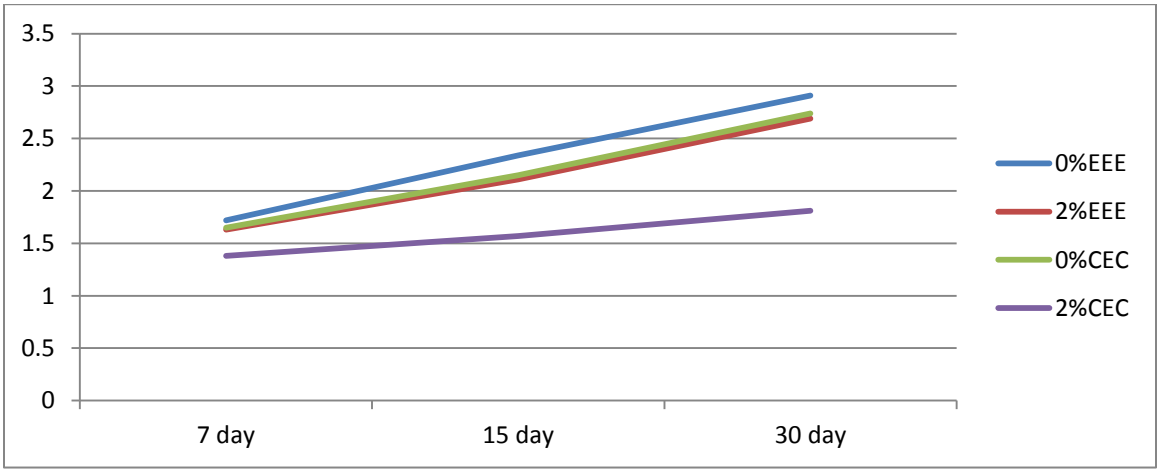


Fig 5.20 Percentage decrease in tensile strength after degradation in water

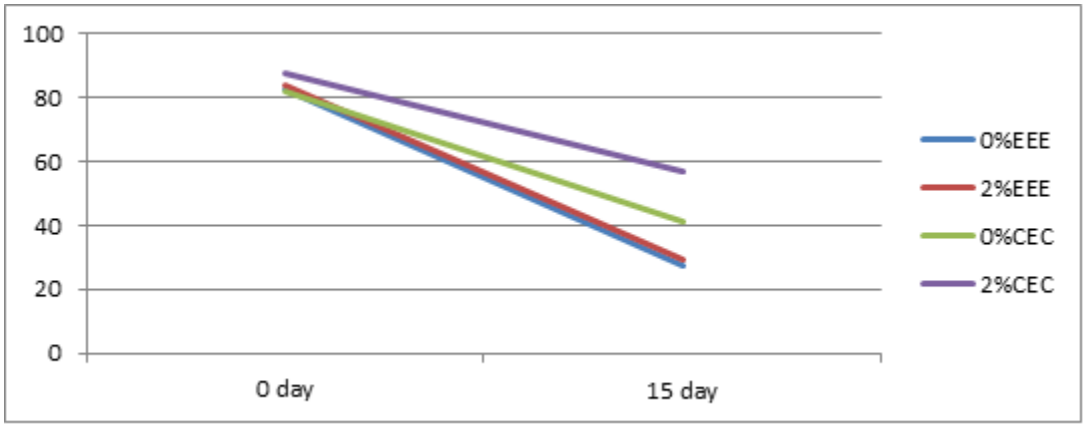


Fig 5.21 Decrease in tensile strength after degradation in NaOH+water

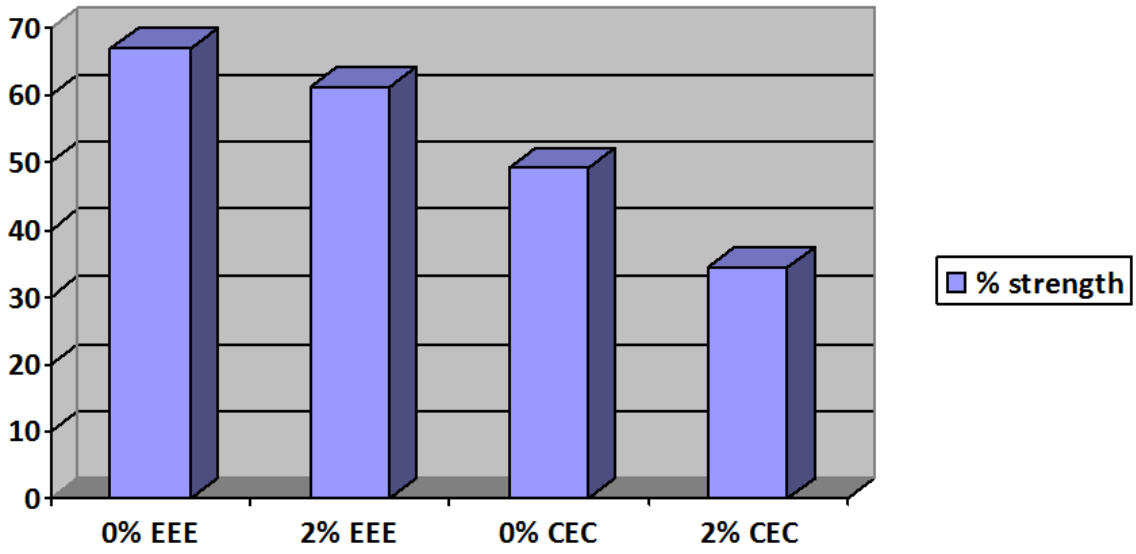


Fig 5.22 Percentage decrease in tensile strength in NaOH+water

After 30 days of water immersion of these specimens, there is sharp decrease in tensile strength. The percent decrease in tensile strength value of specimen having 0 wt% of Nano clay loading and EEE fiber laminates is highest among other specimens. Figure 5.19 & 5.20 shows the effect of water immersion of specimen on tensile strength and Fig 5.21 & 5.22 shows effect of NaOH immersion of specimen on tensile strength. A decrease in strength of all specimens is observed. This may be attributed to the capability of the water molecules to penetrate through the epoxy network. The diffusion of water occurs in epoxy resin was attributed to the nature of the polymer which showed strong interaction with water. In epoxy matrices, water molecules couple strongly with hydrophilic functional groups such as hydroxyl or amine in epoxy resin. The water molecules might interact with epoxy molecules by forming hydrogen bonding with hydrophilic groups. The results are in accordance with the research carried out by Zhou *et al.* The absorption of water could be attributed to the affinity of the functional groups of the epoxies which having high polarity towards water molecules. The results are in accordance with the research carried out by Karad *et al.*

It is also seen that the strength degradation in specimens immersed in NaOH bath was more severe than samples immersed in simple water. A graph of percent decrease in tensile strength and tensile strength degradation as a function of no. of days is shown in Figure 5.21 & 5.22 shows that EEE laminates have maximum percentage of tensile strength decrease as compared to CEC laminates.

5.4.2 Bending test results of the specimens under hygrothermal loading

Table 5.8 & 5.9 showed the bending test results of the samples immersed in water and NaOH for Different days of exposure.

No. of Days	Sample Name	Sample No. Tensile	Modulus (MPa)	Flexural Strength(MPa)	% Decrease in strength
0 Day	0 % EEE	sample No 1	7150	81.7	
		sample No 2	6620	72.71	
		sample No 3	4680	69.85	
		Average		74.75	
	2% EEE	sample No 1	4430	101.25	
		sample No 2	3500	95.42	
		sample No 3	3410	88.68	
		Average		95.12	
	0 % CEC	sample No 1	8170	27.3	
		sample No 2	8580	33.5	
		sample No 3	8472	34.9	
		Average		31.90	
	2% CEC	sample No 1	1135	41.24	
		sample No 2	9128	33.72	
		sample No 3		41.31	
		Average		38.75	
7 Day	0 % EEE	sample No 1	7150	53.46	
		sample No 2	6620	48.76	
		sample No 3	7254	55.56	
		Average		52.593	29.64
	2% EEE	sample No 1	4430	64.75	
		sample No 2	3500	72.98	
		sample No 3	3754	73.68	
		Average		70.47	25.91
	0 % CEC	sample No 1	8170	29.15	
		sample No 2	8580	27.68	
		sample No 3	8472	32.42	
		Average		29.75	6.74
	2% CEC	sample No 1	4430	41.8	
		sample No 2	3500	34.7	
		sample No 3	4278	36.42	
		Average		37.64	2.76
15 Day	0 % EEE	sample No 1	7150	43.16	
		sample No 2	6620	36.34	
		sample No 3	5460	44.19	
		Average		41.23	44.85

	2% EEE	sample No 1	4430	59.76	
		sample No 2	3500	54.49	
		sample No 3	4278	60.56	
		Average		58.27	38.74
	0 % CEC	sample No 1	4430	31.89	
		sample No 2	3500	27.26	
		sample No 3	4430	28.57	
		Average		29.24	8.35
	2% CEC	sample No 1	1840	41.22	
		sample No 2	1682	33.55	
		sample No 3	1742	37.58	
		Average		37.45	3.36
30 Day	0 % EEE	sample No 1	1920	32.35	
		sample No 2	1870	27.6	
		sample No 3	1684	33.45	
		Average		31.45	59.26
	2% EEE	sample No 1	1320	40.15	
		sample No 2	1330	48.6	
		sample No 3	1480	47.64	
		Average		45.13	53.93
	0 % CEC	sample No 1	1456	24.89	
		sample No 2	1620	32.67	
		sample No 3	1358	28.66	
		Average		28.74	10.65
	2% CEC	sample No 1	1769	40.52	
		sample No 2	1685	33.4	
		sample No 3	1498	37.98	
		Average		37.3	4.25

Table 5.8 Flexural test Results of specimens immersed in water bath for different days of exposure at 45 ^{o}C Temp.

0 Day	0 % EEE	sample No 1	7150	81.7	
		sample No 2	6620	72.71	
		sample No 3	4680	69.85	
		Average		74.75	
	2% EEE	sample No 1	4430	101.25	
		sample No 2	3500	95.42	
		sample No 3	3410	88.68	
		Average		95.12	
	0 % CEC	sample No 1	8170	27.3	

		sample No 2	8580	33.5	
		sample No 3	8472	34.9	
		Average		31.90	
		sample No 1	1135	41.24	
		sample No 2	9128	33.7	
		sample No 3		41.31	
	2% CEC	Average		38.75	
15 Day NaOH	0 % EEE	sample No 1	1920	42.35	
		sample No 2	1870	49.02	
		sample No 3	1684	44.26	
		Average		45.21	60.47
	2% EEE	sample No 1	1320	40.15	
		sample No 2	1330	38.64	
		sample No 3	1480	42.86	
		Average		40.55	57.37
	0 % CEC	sample No 1	3680	17.54	
		sample No 2	5060	14.83	
		sample No 3	4876	16.68	
		Average		16.34	48.76
	2% CEC	sample No 1	2320	24.16	
		sample No 2	1880	22.08	
		sample No 3	2154	29.99	
		Average		25.41	34.43

Table 5.9 Flexural test Results of specimens immersed in NaOH + water Bath

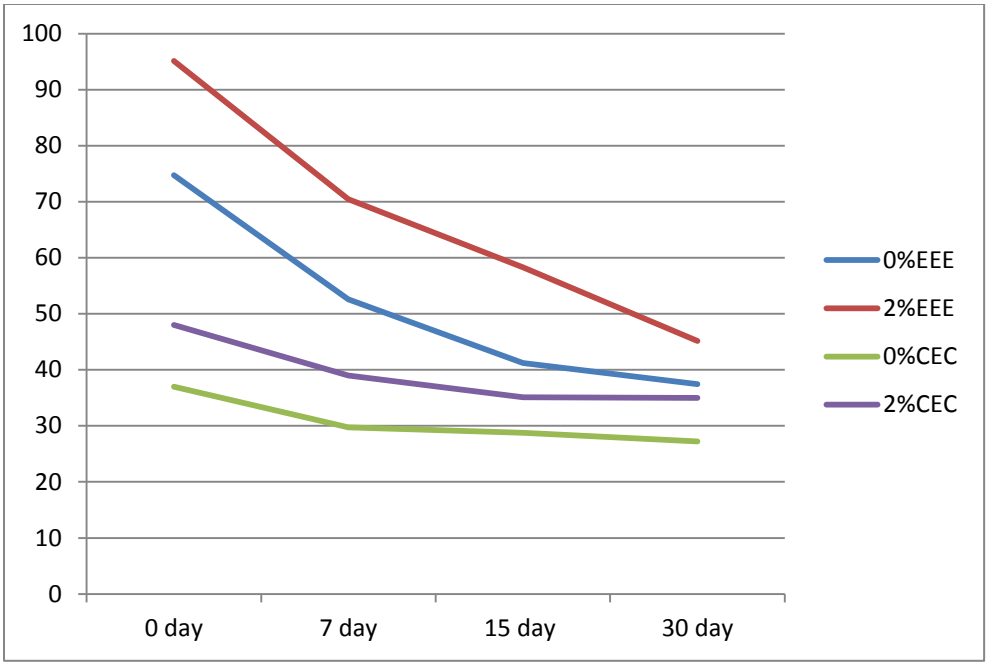


Fig 5.23 Decrease in Flexural strength after degradation in water

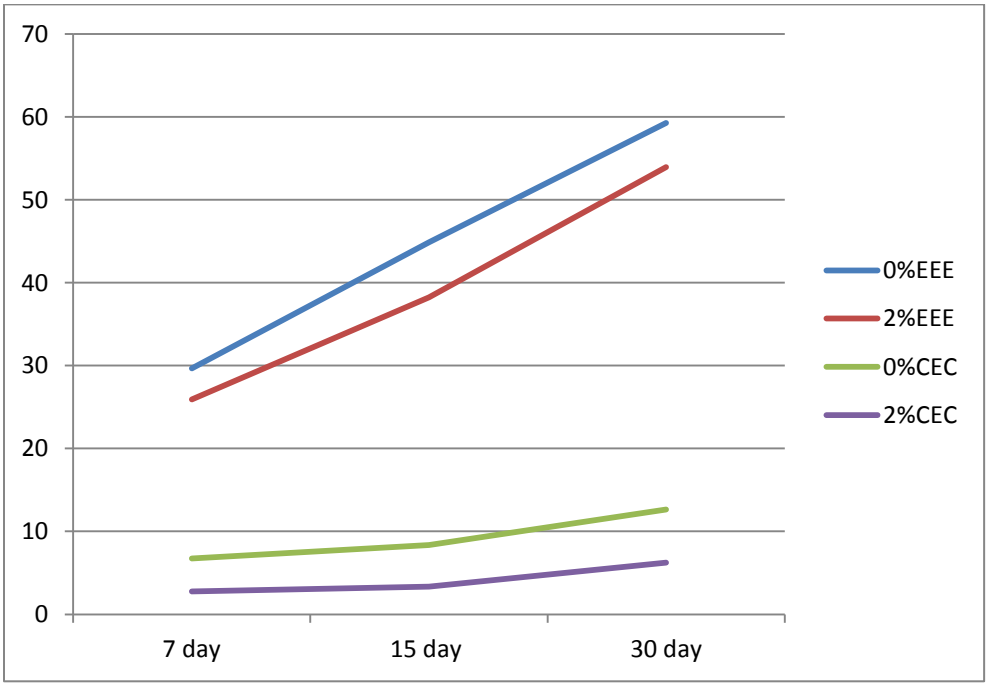


Fig 5.24 Percentage decrease in Flexural strength after degradation in water

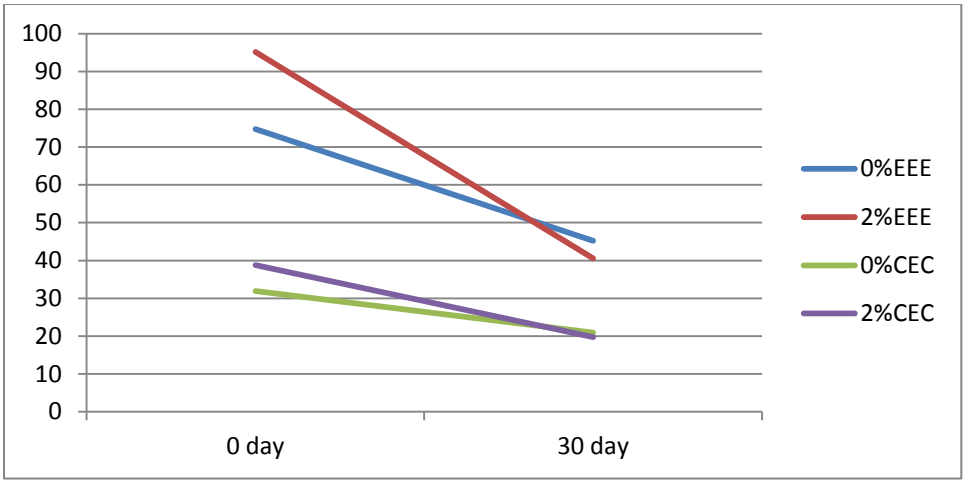


Fig 5. 25 Decrease in Flexural strength after degradation in NaOH+water

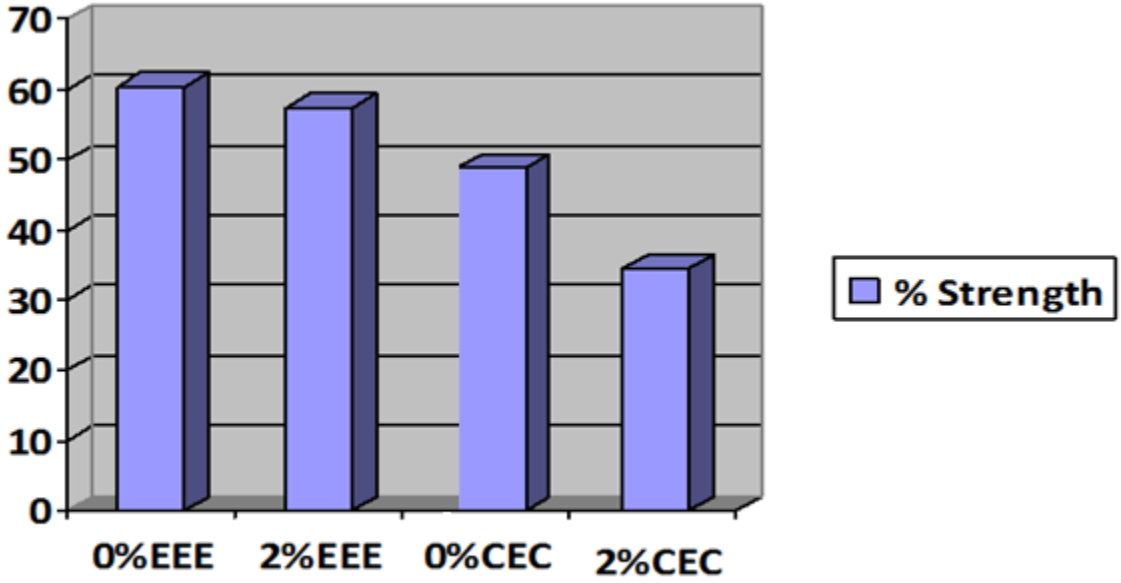


Fig 5.26 Percentage decrease in flexural strength of specimen immersed in NaOH+water

From tables 5.8 and 5.9, the water immersion of 0 wt% EEE specimen results in 59.26% and 2% EEE results in 53.93% decrease in flexural strength in comparison to 0%CEC specimen results in 10.65% and 2% CEC results in 4.25 % decrease in flexural strength . The NaOH immersion of 0 wt% EEE specimen results in 60.47% and 2% EEE results in 57.37% decrease in flexural strength in comparison to 0%CEC specimen results in 34.49% and 2% CEC results in 49.16 % decrease in flexural strength which showed that there is tremendous decrease in flexural strength of specimens immersed in NaOH as compared to specimens immersed in water.

CHAPTER 5

CONCLUSION AND FUTURE SCOPE

Fiber reinforced epoxy nanocomposites were prepared by hand lay-up method, two types of configurations of these laminates prepared i.e.(i) E-glass fiber epoxy laminate (EEE) (ii) E-glass fiber lamina sandwitched between C-glass fiber laminas (CEC) for neat and 2% clay loading. Hygrothermic aging of these two configurations were studied for their suitability in humid applications. The specimens were exposed to water and saline environment at 45^{o} C temp for duration of 7 day, 15 day and 30 days. The specimens were periodically weighted for moisture absorption and tested Mechanical properties (Ultimate tensile strength, flexural strength) & Microscopic behavior. Diffusion mechanism was studied on the basis of Ficks law of diffusion. The results were tested and confirmed by SEM. Microscopic behavior of epoxy laminates studied using Vickers Hardness test, XRD and TEM.

The water absorption increased with increase in immersion time of all Samples. Water uptake is linear and very rapid in the beginning of the exposure after which it slows down and reaches saturation level. The maximum moisture absorption was observed for 0% EEE epoxy laminates and minimum for 2% CEC epoxy laminates. The diffusion coefficient (D) was largest for 0% EEE and lowest for 2% CEC laminates. All Glass fiber epoxy laminates have tendency to absorb more water in saline environment. The velocity of water ingress into these four types of epoxy nanocomposite follows the order 0% EEE > 2% EEE > 0% CEC > 2% CEC . The failure in Nano composites was due to combined effect of matrix cracking, delamination and fibre breakage.

The degradation in mechanical properties is due to the degradation in fibre/matrix interface bonding. The voids present in the matrix are the main reasons for moisture diffusion. The microcracks formed during the composite preparation or by the service condition can store the trapped water.

The tensile and flexural test shows that the percent decrease in strength value of specimen having 0 wt.% of nanoclay loading and EEE fiber laminates is highest among other specimens.

This study conclusion proved that exposure to saline environment is much more deleterious in comparison to the water environment and CEC epoxy laminated are much better alternative to three ply E glass epoxy laminates as far as degradation of components shown under hygrothermal loading.

FUTURE SCOPE

- Hygrothermal study for longer duration 2 Month, 3 Month or 6 Month can be studied to know exact saturation point with minimum error.
- Hygrothermal study for different temperature environment from freezing temperature to boiling temperature and in between intervals can be studied.
- Hygrothermal study of samples for different percentage of clay loading can be studied.
- Specimens can be prepared using different types of fibers in addition to glass fibers such as RCF, cellulose and glass fiber plates etc.
- Anova techniques can be applied to know optimum percentage of clay loading for saturation point of water uptake for different types of samples.
- Samples can be prepared by using new techniques instead of hand lay-up method for better results.
- Hygrothermal study of samples to be studied for exposure to gases, electrical fields and radiation, magnetic fields etc.

REFERENCES

Autar K. Kaw Mechanics of Composite Material, CRC Press , Taylor & Francis pub. ISBN – 13: 978-0-8493-1343-I.

A. Alhuthali, I.M. Low, C. Dong, (2011) Characterization of the water absorption, mechanical and thermal properties of recycled cellulose fiber reinforced vinyl-ester eco-nanocomposites. Composite : Part B S1359-8368(12)00277-6 New york, Elsevier.

Alexandre M, (2000). Polymer-layered Silicate Nanocomposites: Preparation, Properties and uses of a New Class of Materials. Mater. Sci. Eng. Rep., 28, 1-63. [1]

Avila A, Horacio V. and Marcelo I. (2005). The nanoclay influence on impact response of laminated plates. Latin American journal of solids and structures, 3, 3-20.

Avila A, Almir S and Marcelo I. (2006). A study on nanostructured plates behavior under low-velocity impact loading. Material and design, 34, 28-41.

A. Kootsookos, A.P. Mouritz (2004), Seawater durability of glass- and carbon-polymer composites, Composites Science and Technology, 64, 1503–1511.

Berketis K, Tzetzis D and Hogg P.J, (2007). The influence of long term water immersion ageing on impact damage behaviour and residual compression strength of glass fiber reinforced polymer (GFRP). Material and design, 29, 1300-1310.

Biron, M. (1973). Thermosets and Composites-Technical Information for Plastics Users. New York: Elsevier.

Chow W, Bakar A and Ishak Mohamad A. , (2005). Water absorption and hygrothermal aging study on organomontomorrillonite reinforced polyamide6/polypropylene nanocomposites. Journal of applied polymer science, vol 98, 780-790.

Fatemeh Ravari , Abdollah Omrani a, Abbas Ali Rostami a, Morteza Ehsani (2012) Ageing effects on electrical, morphological, and mechanical properties of a low viscosity epoxy nanocomposite, Polymer Degradation and Stability, 97 929-935 Newyork, Elsevier.

F. A. Ramirez, L. A. Carlsson, B. A. Acha (2008), Evaluation of water degradation of vinylester and epoxy matrix composites by single fiber and composite tests, J Mater Sci, 43,5230–5242.

Frederick T. Wallenberger, James C. Watson, and Hong Li, PPG Industries,

Inc. (2001) Glass Fiber ASM Handbook, Vol. 21: Composites (#06781G).

Gopalan R, Somashekar BR, Environmental effects on fiber-polymer composites, *Polym Degrad Stabil*, 24, 361-371, 1989.(5.2.1)

Gao Shang-Lin, Mader E and Plonka R., (2007). Nanocomposite coating for healing surface defects of glass fiber and improving interfacial adhesion. Composite science and technology, 68, 2892-2901.

Hossain M. K., Imran K. A., Hosur M. V. and Jeelani S.,(2011). Degradation of Mechanical properties of convectional and nanophased Carbon/Epoxy composites in seawater. Newyork , Elsevier.

H. Alamri, I.M. Low, (2012) Mechanical properties and water absorption behaviour of recycled cellulose fibre reinforced epoxy composites. Polymer Testing 31 620–628

New york, Elsevier.

Jang-Kyo Kim, Chugang Hu, Ricky S.C Woo, Man-Lung Sham (2005), Moisture barrier characteristics of organoclay–epoxy nanocomposites, Comp. Sci. and Tech., 65,805-813.

Jena P, (1996). Nanostructured materials. Nova Science New York 1996.

Karad S. K., Attwood D., (2005), Jones F. R.: Moisture absorption by cyanate ester modified epoxy resin matrices, Part V: Effect of resin structure, Composites: Part A, 36, 764–771.

Klaus D.Sattler - Handbook of Nanophysics , CRC Press ISBN 978-1-4200-7552-6

Kornmann X, Rees M, Thomsan Y, Necola A, Barbezat M and Thomsan R, (2005). Epoxy layered silicate nanocomposite as matrix in glass fiber-reinforced composites. Composite science and technology, 65, 2259-2268.

Kudamara S Rai, and Jeena J Karippal , (2009) Hygrothermic Behaviour of Carbon /Vinylester, Glass/Vinylester, Carbon/Epoxy and Glass/Epoxy Composites. Iranian Polymer Journal 19 (2), 2010, 89-103

Lei Wang, Ke Wang, Ling Chen, Chaobin He, (2006) Hydrothermal Effects on the thermomechanical properties of high performance epoxy/ clay nanocomposites,poly. engg. and sci,

Lei Wang, Ke Wang, Ling Chen and Chaobin He, (2006). Hydrothermal Effects on the Thermo-mechanical Properties of High Performance Epoxy/Clay Nanocomposites. Polymer engineering science, 46, 215–221.

Lowenstein, K. L. (1973). Manufacturing Technology of Continuous Glass Fibers. New York: Elsevier.

Masami Okamoto, (2003) Polymer/Layered Silicate Nanocomposites Rapra review reports publication ISBN: 1-85957-391-6

Manjunatha C.M, Taylor A.C, Kinloch A.J and Sprenger S, (2009). The tensile fatigue behavior of a silica nanoparticle-modified glass fiber reinforced epoxy composites. Composite science and technology, 70, 193-199.

Nanostructured and quantum effects (H Sakaki and H. Noge, eds) Springer Verlag, Berlin (1994).

Njuguna J and Pielichowski K, *Advanced Engineering Materials*, 5, 769 (2003).

Quaresimin M. and Varley R. J, (2007). Understanding the effect of nano-modifier addition upon the properties of fibre reinforced laminates. Composite science and technology, 68, 718-726.

Rumiana Kotsilkova, Thermoset Nanocomposites for Engineering Applications, Smithers Rapra Technology Limited publication ISBN: 978-1-84735-062-6

S. T. Peters, Handbook of Composites, Chapman & Hall, 810-821.

Sreejith Muthirakkal, H N R Narasimha Murthy, Munishamaiah Krishna,(2009) Hygrothermic Behaviour of Carbon/Vinylester,Glass/Vinylester, Carbon/Epoxy and Glass/Epoxy Composites Iranian Polymer Journal 19 (2), 2010, 89-103.

Sinha R. S., Okamoto M., (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog. Polym. Sci., 28, 1539–1641.

Wang H, Zeng C, Elkovitch M and Koelling W. K, (2001). Processing and properties of polymeric nanocomposites. Polymer engineering and science, 41, 11.

Wetzel B, Rosso P, Haupert F and Friedrich K, (2006). Epoxy nanocomposite-fracture and toughening mechanisms. Engineering fracture mechanics, 73, 2375-2398.

Y.J. Weitsman, (1995), Effects of fluids on polymeric composites: a review, technical report.

Y.J. Weitsman, M. Elahi, (2000), Effects of fluids on the deformation, strength and durability of polymeric composites – An Overview, Mechanics of Time-Dependent Materials, 4, 107–126.

Yasmin A, Luo J.J, Abot J.L, Danial I.M, (2006). Mechanical and thermal behavior of clay/epoxy nanocomposites. Composite science and technology, 66, 2415-2422.

Zainuddin S, Hosur M.V, Zhou Y, Kumar Ashok and Jeelani S, (2010). Durability study of neat/nanophased GFRP composite subjected to different environmental conditioning. Material science and engineering, A 57, 3091-3099.

Zhou J., Lucas J. P., (1999), Hygrothermal effects of epoxy resin. Part 1: The nature of water in epoxy. Polymer, 40, 5505–5512.