EFFECT OF FIBER SURFACE TREATMENT ON MECHANICAL PROPERTIES OF CARBON FIBER REINFORCED COMPOSITES

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

Master of Engineering

in

Production Engineering

by

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July, 2015

CERTIFICATE

This is certify that the work done in this dissertation entitled "**EFFECT OF FIBER SURFACE TREATMENT ON MECHANICAL PROPERTIES OF CARBON FIBER REINFORCED COMPOSITES**" submitted in partial fulfilment of requirements for the award of Master of Engineering degree in Production Engineering in Department of Mechanical Engineering of Thapar University, Patiala, is an authentic record of work carried out by me under the guidance of **Mr. Bikramjit Sharma,** Assistant Professor, Department of Mechanical Engineering and **Dr. Rajeev Mehta,** Professor, Department of Chemical Engineering, Thapar University, Patiala.

The matter embodied in this dissertation has not been submitted in part or full to any university or institute for the award of any degree.

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This is certified that the above statement made by the student is correct to the best of our knowledge and belief.

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ABSTRACT

In this work, different surface treatments: viz. Acetone desizing, nitric acid treatment, silane treatment, nitric acid treatment followed by silane treatment are performed on carbon fibers. The modified carbon fibers are embedded in epoxy matrix and high quality 2-ply laminated composites are manufactured using vacuum bagging method. The interlaminar shear strength, flexural strength and flexural modulus of composites are improved by treatments. The chemical bonds formed between carbon fibers and epoxy matrix as a result of silanization gave better results as compared to the mechanical interlocking between carbon fibers and matrix induced by etching using nitric acid. A significant improvement in interlaminar shear strength (11 MPa) and flexural strength (488 MPa) of composites is achieved by treating the fibers with nitric acid for 5 minutes followed by silane treatment using 3-Aminopropyl-trimethoxy silane. This is attributed to creation of active sites and hydroxyl (-OH) groups on fiber surface by nitric acid treatment which improved bonding between silane and carbon fibers.

Table of Contents

Contents **Page No.**

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

List of Figures

List of Tables

List of Graphs

List of Equation

ABBREVIATIONS

ASTCF	Amino silane treated carbon fiber
ATCF	Acetone treated carbon fiber
CF	Carbon fiber
CFRP	Carbon fiber reinforced polymer composite
ESTCF	Epoxy silane treated carbon fiber
FTIR	Fourier transform infrared spectroscopy
MAPP	Maleic anhydride graphted polypropylene
NCF	Neat carbon fiber
NA5ASTCF	Nitric acid (5 min.) and amino silane treated carbon fiber
NA15ASTCF	Nitric acid (15 min.) and amino silane treated carbon fiber
NA5TCF	Nitric acid (5 min.) treated carbon fiber
NA15TCF	Nitric acid (15 min.) treated carbon fiber
NA30TCF	Nitric acid (30 min.) treated carbon fiber
RTM	Resin transfer molding
SEM	Scanning electron microscope
SMC	Sheet molding compound
VARIM	Vacuum assisted resin infusion molding
XPS	X-ray photo emission spectroscopy

CHAPTER 1

Introduction

1.1 Fiber reinforced composites

Fiber-reinforced composites are relatively new range of materials and it has arrays of applications in different industries. Fiber reinforced composite have strong fibers bonded with matrix in such a way that although both continued to have their physical and chemical properties intact, their arrangement and combination renders completely new sets of properties, different from parent materials. Fibers basically acts as load carrying members and matrix assists to uniformly distribute the load among the fibers as well as keep the fibers at their specific location.

Coupling agents are used to enhance the wet ability of matrix and interfacial adhesion between fiber and matrix. Fillers give dimensional stability to the structure and also to cut-off some cost.

The first step in manufacturing is to combine legions of fibers to form a one thin sheet of matrix called lamina. The thickness of a lamina ranges between 0.1–1mm.Several lamina can be stacked to manufacture a laminate, which has applications in many engineering structures.

1.2 Fibers

Fibers are chief constituent in composite materials as they carry a massive majority of the load on a composite structure. The choice of fiber depend on the application of composite as it affects various characteristics of composite such as specific gravity, tensile modulus, fatigue strength and others.

1.2.1 Glass fibers

Glass fiber is most popularly used fiber because of its low cost and high chemical resistance. The chief component in glass fibers is silica and other oxides like boron oxide and aluminum oxide.

1.2.2 Carbon fibers

Carbon fibers are used when high tensile strength-weight ratio and tensile modulus-weight ratio is needed. Due to its high cost it is used in only selective industries like aerospace.

1.2.3 Boron fibers

Tungsten wire is commonly used material for the production of boron fibers. Alike carbon fibers, they have also high cost and hence only used in aerospace industry due to its high resistance to buckling and high compressive strength.

1.2.4 Silicon carbide fibers

Silicon carbide fibers are generally thick fibers and used in the manufacturing of metal and ceramic-matrix composite.

1.3 Matrix

The basic purpose of the Matrix is to distribute stresses between the fibers and to acts as a shield against environment damages like temperature. The matrix also prevents fiber from buckling under compressive loading.

1.3.1 Polymeric

A. Thermoset polymers(resins)

- Epoxies: used in aerospace industry.
- Polyesters, vinyl esters: used in electrical, chemical and automobile industries.

B. Thermoplastic polymers

- Nylons, Polycarbonate, Polyacetals, Polyamide-imides, Polyphenylene sulfide.

1.3.2 Metallic

- Aluminum and its alloys, titanium alloys, magnesium alloys and stainless steel.

1.3.3 Ceramic

- Aluminum oxide, silicon carbide, silicon nitride.

1.4 Defects in composites

- ➢ **Porosity** This defect basically arises due to the presence of volatile component in resin or due to the entrapment of air during curing process.

- **Fiber misalignment** The total volume fraction is affected due to the deviation from ideal packing of fibers.
- **Ply misalignment** This defect occur due to error made in lay-up of the component plies which consequently affect the net stiffness and strength.
- **Ply cracking** Thermal cracks are induced in certain ply of lay-up due to differential contraction.
- **Fiber defects** When the defect is present in fiber, it can adversely affect the strength and other properties of the composite.
- **Delamination** Sometimes a repeated stress or an impact can cause the layers of material to separate which results in the overall low mechanical toughness.

1.5 Detection methods

1.5.1 Ultrasound method This is most commonly used methods for the inspection of composite. The velocity and intensity of ultrasonic pulse through material reveal the basic physical properties of structure. Due to highly dispersive nature of composite, there is great loss of intensity of ultrasonic waves. The velocity and loss of intensity is dependent on frequency. The characteristics of ultrasound waves may influence by composite structure, defects and damage.

1.5.2 Thermal imaging In this method, the heat flux is applied across structure and any discrepancy in the temperature distribution reveals the defects in the material. When the thermal conductivity of material is high, testing frequency higher than 5Hz is needed.

1.5.3 Radiography In this technique, a beam of radiation is bombarded on the surface of the material and the intensity of beam is recorded when it came out of the other end. The internal defects appear as a shadow images on the photographic film. X-rays are commonly used for this purpose. However, if material is thick, gamma rays are used because of its shorter wavelengths.

1.5.4 Acoustic emission In this method, elastic stress waves is applied across material and piezoelectric transducers attached on the surface of material measure the resultant stress level of wave after being travel through material. If the applied stress level is low, these failure modes are likely to occur at the sites of defects and by monitoring the acoustic emission, we can locate the defects in the material.

1.6 Advantages of composite material

- Possess excellent specific strength and specific stiffness characteristics
- Easy machinability
- High resistance to corrosion, chemical damage and other environmental conditions
- Better dimensional stability due to low coefficient of thermal expansion
- High damping capacity.

1.7 Applications of composites

- Used in production of aerospace devices and space technology
- Used in racing cars, bicycle frames and other sports goods
- Extensively used in engineering and industrial field
- Used in transport vehicles, especially for high speed and fuel efficient transports.

1.8 Carbon Fibers

Carbon fiber consists of mixture of amorphous and graphitic carbon. In graphitic form, carbons are arranged in crystallographic structure of parallel plane and this arrangement renders high tensile modulus. The carbon atoms in each plane are arranged at corners of regular hexagon with strong covalent bonds. However, the bond between the planes is much weaker due to Vander wall forces. This arrangement as shown in Fig 1.1 and Fig 1.2, give rise to high anisotropic physical and mechanical property for the carbon fiber.

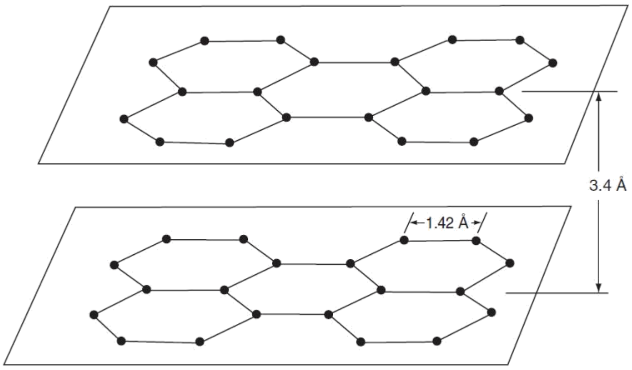


Fig. 1.1 Alignment of carbon fiber [4]

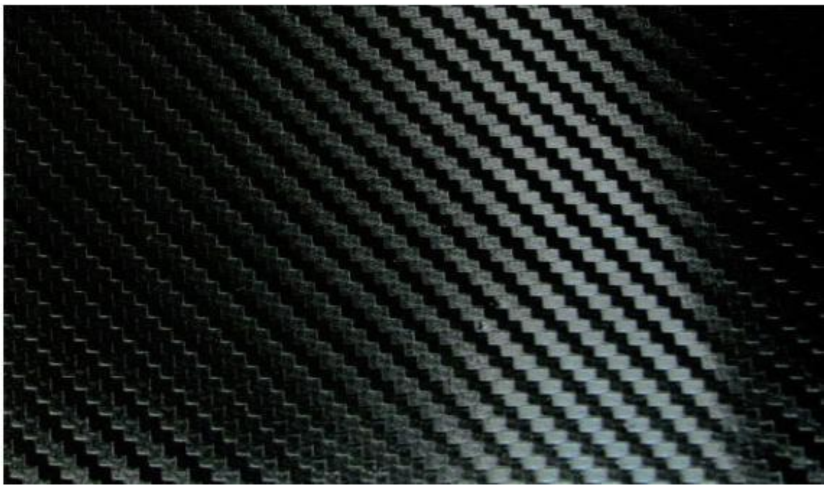


Fig. 1.2 Carbon fiber [5]

The basal plane in carbon are along the fiber axis but alignment can be either be circumferential, radial, random or combination of all in transverse direction. The thermo elastic property and coefficient of thermal expansion depends on the type of arrangement.

Carbon fibers are basically manufactured from two types of material:

1. Textile precursors
2. Pitch Precursors

The most widely used textile precursors is polyacrylonitrile (PAN). It consists of polar group that can be arranged either side of the chain. PAN filaments are obtained by wet spinning of solution and stretched at an elevated temperature during which chains are aligned in filament direction further PAN filaments are carbonized by heating at 1000-2000°C in an inert environment during this process oxygen and nitrogen atoms are removed and filament is arranged in an aromatic ring patterns in parallel plains. After that carbonized filaments is further heated above 2000°C and their structure becomes more ordered, now graphite filament has high tensile modulus but low tensile strength which can be increased by stretching them above 2000°C

Pitch is by product of petroleum refining and the carbon atoms in this are arranged in an aromatic ring pattern and by heating it above 300°C it changes to long two dimensional sheets like structure. This stage is known as mesophase. After melts spinning mesophase pitch through a spin rate, pitch filament is produced. This filament is then carbonized at temperature around 2000°C and rest of the process is similar to that of PAN precursors.

After fiber manufacturing process sizing is done on carbon fiber in which organic film is applied on the surface of the fiber to protect its structural part and components. The range of the sizing is 0.5-1.15wt%.Sizing also prevent damage of fiber surface, lubricate the fibers, give anti electrostatic property to fiber, and serve as chemical link between fiber surface and matrix.

Carbon Fibers are available in three forms:

1. Long and continuous tow
2. Chopped (6-50 mm long)
3. Milled (30-3000µm long)

There is no net effect of sizing on the mechanical properties of composite.

1.9 Chemical treatment of carbon fibers

The basic purpose of surface treatment is to improve the fiber matrix interface bonding. The surface treatment of carbon fiber can be classified in two categories.

1.9.1 Oxidative treatments

- Dry oxidation
- Plasma etching
- Wet oxidation
- Anodic oxidation

1.9.2 Non oxidative treatment

- Whiskerization
- Plasma deposition

1.9.1 Oxidative treatments

1.9.1.1 Dry Oxidation

Dry oxidation is generally carried out with air and oxygen or mixture of oxygen and other gaseous mixture like ozone and carbon dioxide at low temperature. The dry oxidative treatments at high temperature reduce the fiber tensile strength. In this process pits are created on the surface layer of the fiber, which give rise to high surface rugosity. The oxides of metallic impurities like copper and lead can enhance the degradation rate of carbon fiber.

1.9.1.2 Plasma Etching

This method is also known as electric discharge treatment and is one of the most popular methods to increase the fiber matrix adhesion. Plasma is fourth state of matter which constitutes positively and negatively highly charged particles. The plasma is created by directing the high energy beam to gases or air. The principle of plasma treatment is to cause the formation of active species in gas like electrons, ions and ionized atoms. The active species of oxygen and fluoride interact with the surface, leads to abstraction of material from surface. On the contrary, active species of hydrogen and fluorocarbon leads to deposition or grafting. The most commonly used plasmas are thermal plasma, glow discharge and corona discharge.

1.9.1.3 Wet oxidation

Wet oxidation incorporates the use of liquid phase oxidizing agent such as nitric acid, acidic potassium permanganate, acidic potassium dichromate, dichromate permanganate, hydrogen peroxide, ammonium bicarbonate. As this treatment is milder than dry oxidation, it has more fiber strength than the latter. However fiber strength depends on various factors such as concentration, expose time, temperature and mode of treatment.

1.9.1.4 Electrolytic or Anodic oxidation

Anodic oxidation is commonly used for the treatment of mass carbon fiber because it is fast and uniform. In this method material is dissolved in the electrolyte of alkaline solution during which formation of carbon dioxide and degradation of product occur simultaneously. The major advantage of this method is that fibers are produced with nominal weight loss.

1.9.2 Non oxidative treatment

1.9.2.1 Whiskerization

Whiskerization is nucleation process in which high strength single crystals of chemical compound such as silicon carbide and titanium dioxide are grown on the surface of fiber perpendicular to the fiber axis.

1.9.2.2 Plasma polymerization

This process includes polymerizable organic vapors like polyamide, polyimide, organosilanes, and propylene. This process swells the surface polar free energy of carbon fiber. The polymer used in this treatment has capacity to fix on fiber surface as well as on resin in matrix.

1.10 Effect of oxidative treatment on carbon fibers

The various surface oxidative treatment methods enhance ILSS, flexural, tensile and compressive strength of the composites. The surface treatment increases the surface area of the fiber by forming pits which consequently elevate the mechanical properties of the composites and interpenetration between matrix and fiber. A light surface treatment methods like electrolytic increase the fiber strength but on the other hand plasma etching cause excessive removal of surface layer, significantly reducing the fiber diameter. The oxidative treatment increases the oxygen and nitrogen content on the fiber surface which leads to better bonding between fiber and matrix. It also increases the wet ability of carbon fiber.

Overall, surface treatment increase fiber surface area, remove weak surface layer, increase surface polar energy and produce carboxyl, hydroxyl and carbonyl groups on the surface of the fiber. If surface treatment is in excess, then it will decrease bond strength and adversely affects other properties of fibers.

1.11 Effect of silane coupling agent on carbon fiber

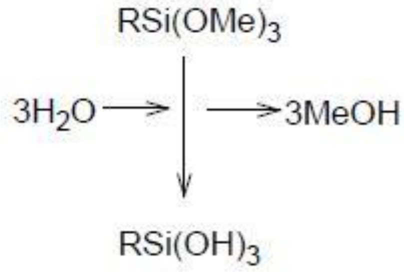
Silane coupling agents are compounds, containing functional groups which are helpful in forming durable bond between organic and inorganic material. The general formula for silane coupling agent reveals two classes of functionality.

$$\mathbf{R\text{-}(CH_2)n\text{—}Si\text{—}X_3}$$

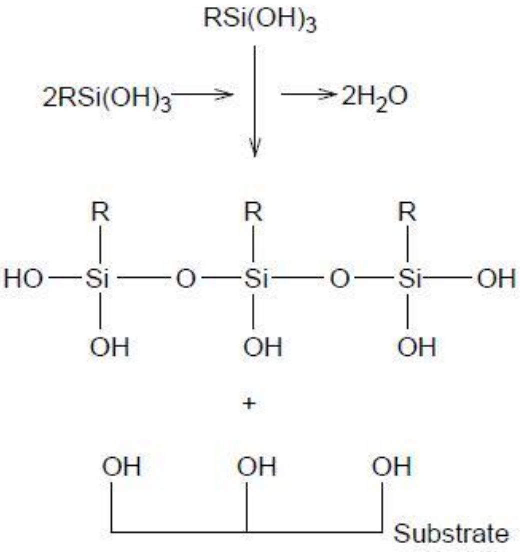
Where X is the hydrolyzable group (alkoxy, halogen and amine). R is a non-hydrolyzable organic radical that may possess functionality which is helpful in binding the organic resin and polymers. CH_2 is linker and Si is silicon atom.

Reaction of silanes is carried out in four steps:

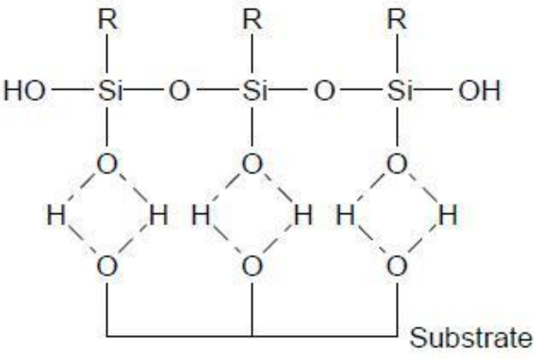
- Intially, hydrolysis of three labile X groups attached to silicon occurs.



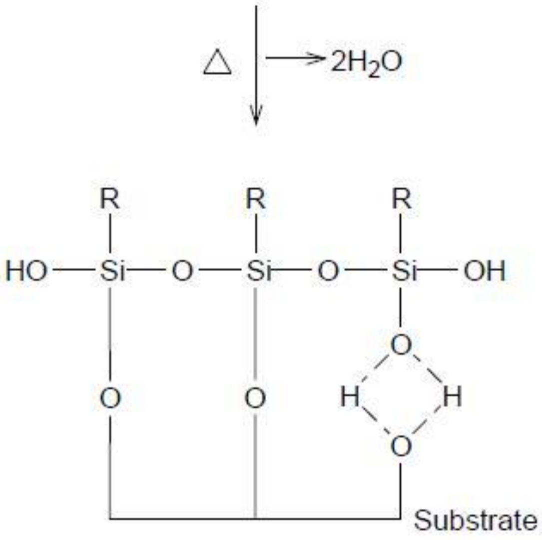
- Condensation to oligomers.



- Hydrogen bond is formed between the oligomers and the substrate.



- During curing process covalent bond is formed with the substrate. At the interface, there is usually one bond from each silicon atom of the organosilane to the substrate surface.



1.12 Manufacturing processes in composites

There are two fundamental manufacturing processes for manufacturing composites.

1. Open molding
2. Closed molding

The choice of manufacturing process depends upon the cost, material, size and volume.

1.12.1 Open molding

The major step in the open molding process is filling the fiber reinforced with resin in open environment, then amalgamating the laminate using manual rollout techniques. The transfer of resin from storage tank to mold is paramount factor in this process. Further there are three types of open molding process.

Hand lay up

In this method single cavity mold is used, gel coat is applied to mold manually and after the gel coat has cured carbon fiber reinforcement is placed on mold and another layer of carbon reinforcement is added to it. This method is suitable for making arrays of composite product like tanks, auto components, bath ware etc. The major advantages of this method are that it posts low cost, simple processing, flexibility in design change and nominal investment.

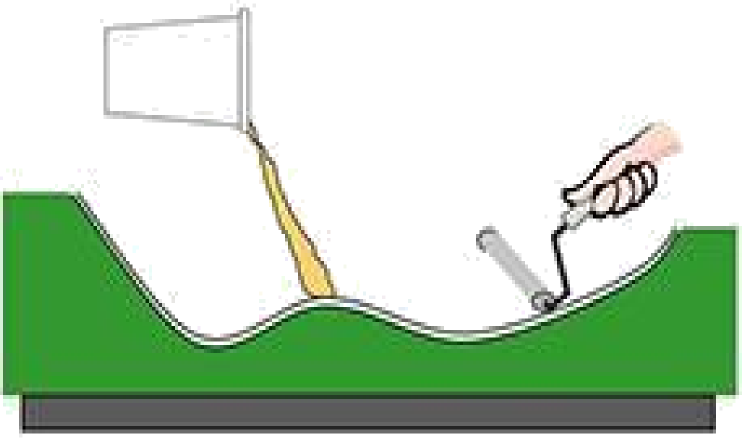


Fig 1.3 Basic Hand lay-up [6]

Spray up

Alike hand layup method, single cavity mold of carbon composite is used. In this process gel coat is applied to mold before spray up of laminate and then laminate is rolled to fill the carbon strand. Subsequent layer of laminate is added to increase its thickness. The major advantages of this method are portable equipment, wide range of parts and low cost tools.

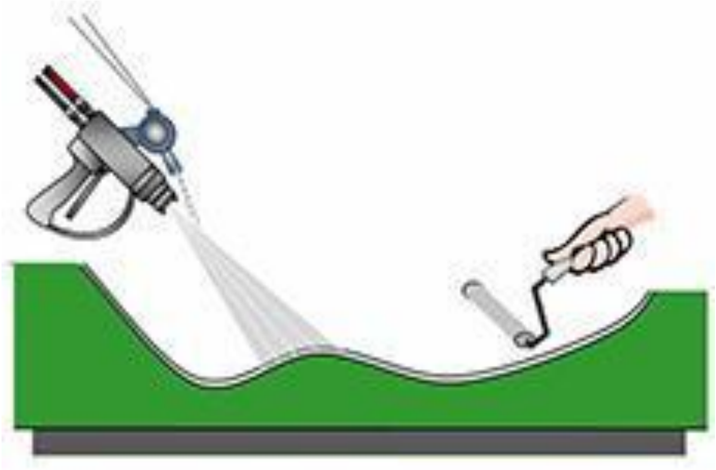


Fig 1.4 Basic spray up [6]

Filament winding

As shown in the Fig 1.5, it is an automated process in which single filament is wrapped around rotating mandrel to manufacture axisymmetric hollow parts. These fibers roving's then go through different process like liquid resin bath containing liquid resin, catalyst, pigments and UV absorbers. The fiber guides located between creel and resin bath control fiber tension.

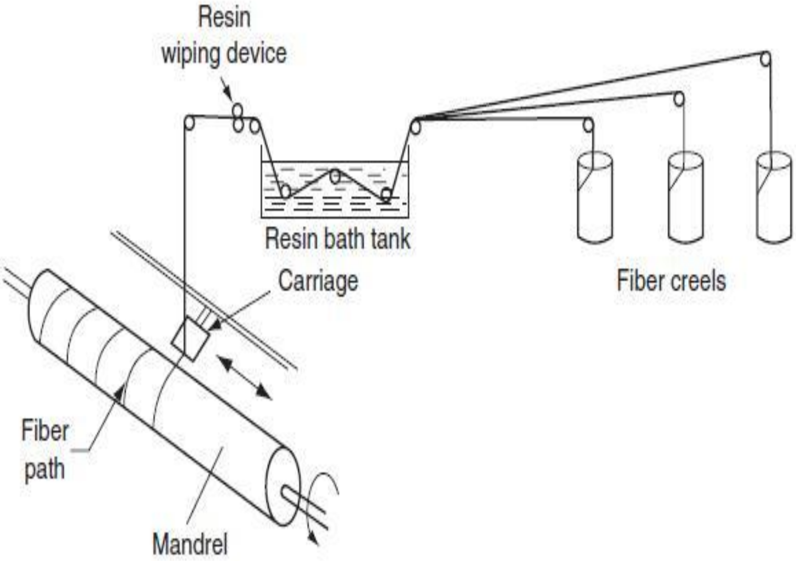


Fig 1.5 Filament winding [4]

The roving’s gathered into a band by passing them through stainless steel comb before entering into resin bath. After passing through resin tank , roving are passed through wiping device which is generally a set off squeeze rollers , whose basic function is to remove excess resin from the roving and control resin coating thickness. Sequently, resin impregnated roving’s are gathered in flat band which can be done by using a straight bar , ring or comb and then positioned on the mandrel through carriage which moves back and forth parallel to mandrel. The two basic parameters of this process is speed of the carriage and binding speed of mandrel, which can manipulated to get desired angle binding patterns.

Pultrusion process

This method is generally used to fabricate long straight members of constant crosssectional area such as solid rods, hollow tubes, flat sheets and beams. The pultruded product comprise of longitudinal aligned continuous strand roving.

As shown in Fig 1.6, first continuous strand roving and mats are pulled from one end of the line into resin bath which contain the mixture of liquid resin, curing agent, UV stabilizer and fire retardant. After that fiber resin is directed to the surface veil, where the thermoplastic polyester is added to fiber resin to enhance its smoothness. Sequently, the fiber resin stream is passed through performers which evenly distribute the fiber bundles and remove excess resin. At last, fiber resin is passed to the die where final shaping, compaction and curing take place and then pulled out by pulling rollers, cooled and cut to the required length by the diamond impregnated saw. The die is heated by oil heater or by electric heater.

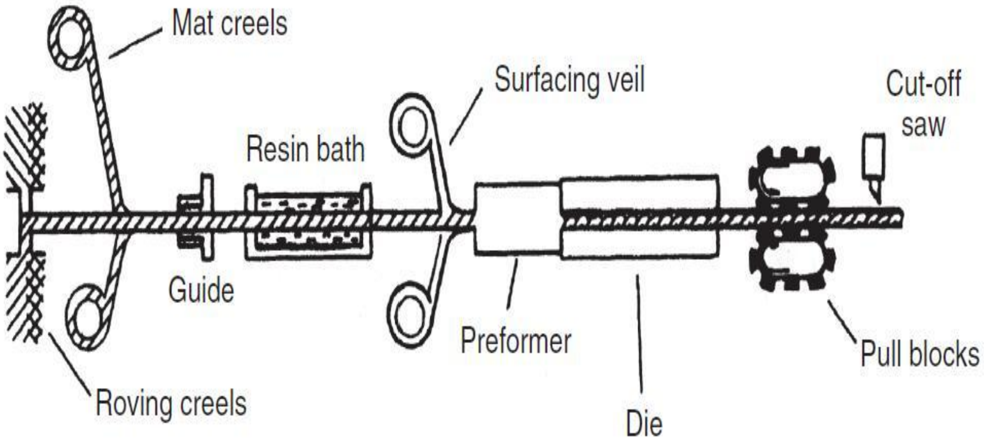


Fig 1.6 Pultrusion process [4]

1.12.2 Closed molding

Compression method

In this process a pre-cut and weighed amount of SMC is placed onto bottom half of the mold cavity. Further this mold is closed quickly and top half is lowered which exert the pressure on the charge. Due to this pressure the charge begins to flow and fill the cavity and entrapped air is removed from the mold. The molding pressure and temperature ranges from 1.4 to 34.5 MPa at 130-160°C respectively. When the desired level of cure is achieved the mold is opened and part is removed. The main advantage of compression molding is ability to make complex geometry.

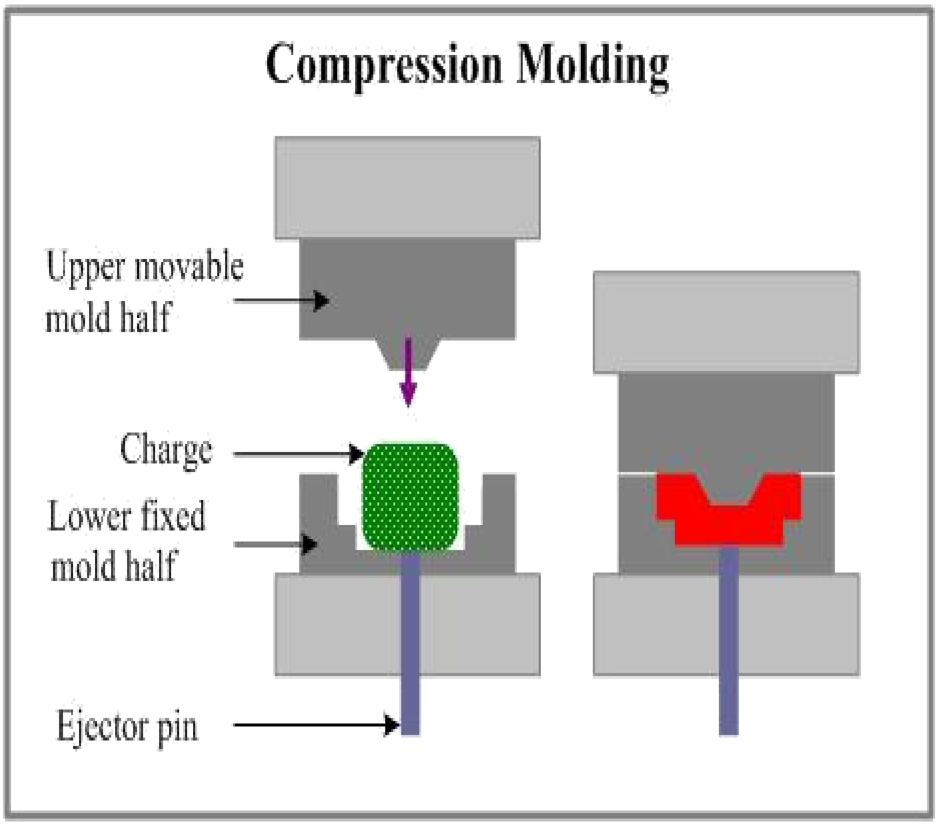


Fig 1.7 Compression molding [5]

Bag molding process

In this process Fig 1.8 shows, prepreg is used as starting material which contains fibers in partially cured epoxy resin. During molding process, the excess resin flow out of the prepreg which displaces the entrapped air and consequently reduces the void content in the laminate. In next step, mold surface is covered with Teflon coated glass fabric separator and prepreg plies are laid upon it at the required angle.

The pressure is applied to attach the prepreg to Teflon coated glass fabric. After this operation, porous cloth and bleeder paper are placed on the prepreg stack to absorb excess of resin. Further, lay up is covered with the sheet of Teflon coated glass fabric separator, a cauls plate and thin heat resistant vacuum bag.

Following this, complete assembly is placed in autoclave where the different plies consolidate and unite into solid laminate by the application of external pressure and vacuum. The curing is done in two stages in this process. In first stage, cure temperature is increase up to 130°C and is maintained at the same for approximately 60 minutes to decrease the resin viscosity. In the second stage autoclave temperature is elevated to actual curing temperature and maintained for two hours to achieve desired level of cure. This method is widely used in aerospace industry where quality is given consideration.

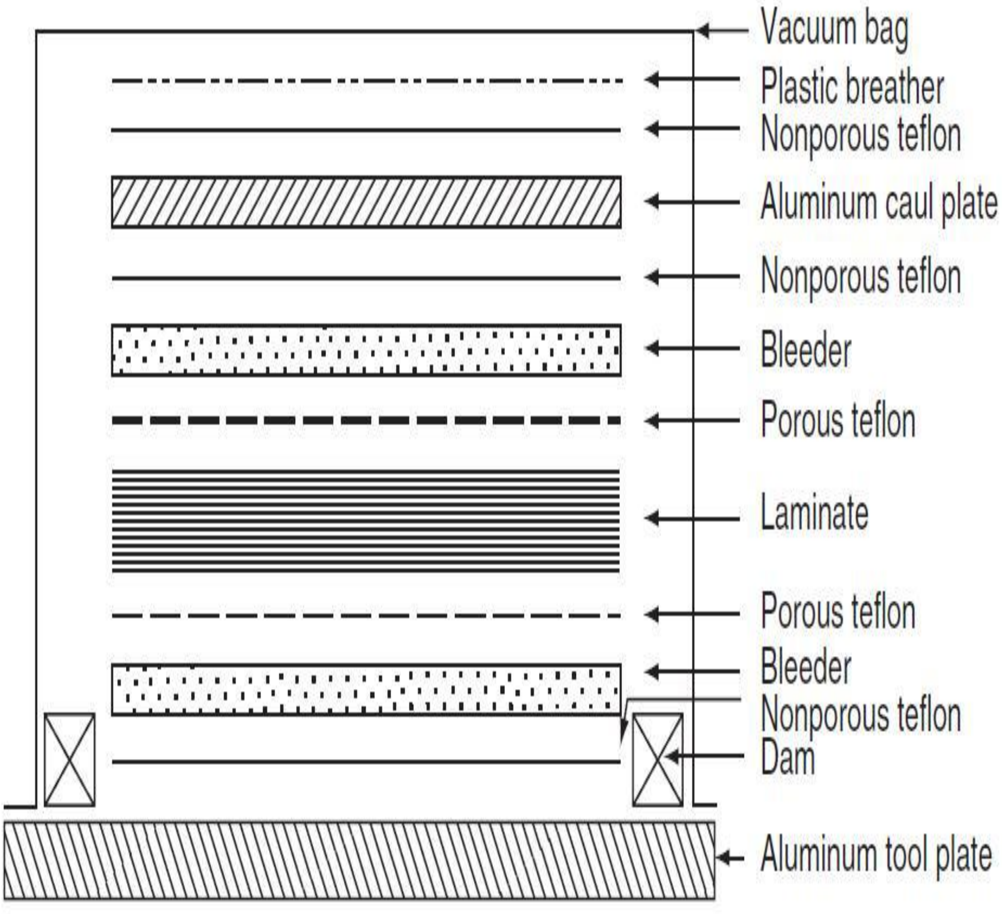


Fig 1.8 Bag molding process [4]

1.12.3 Other manufacturing processes

- RTM
- Elastic reservoir molding
- Tube rolling

RTM

In this method mold is made in two parts i.e. top part and bottom part. First of all plethora of dry continuous strand or cloth are placed on the bottom half of the mold, after the mold is closed a catalyzed liquid resin is injected into mold at pressure ranging of 69-690 kPa through sprue which is located at the lowest point of the mold cavity. Sequent, the liquid resin permeates the fiber on an entrapped air is displaced by resin. The Fig 1.9 shows the basic RTM process.

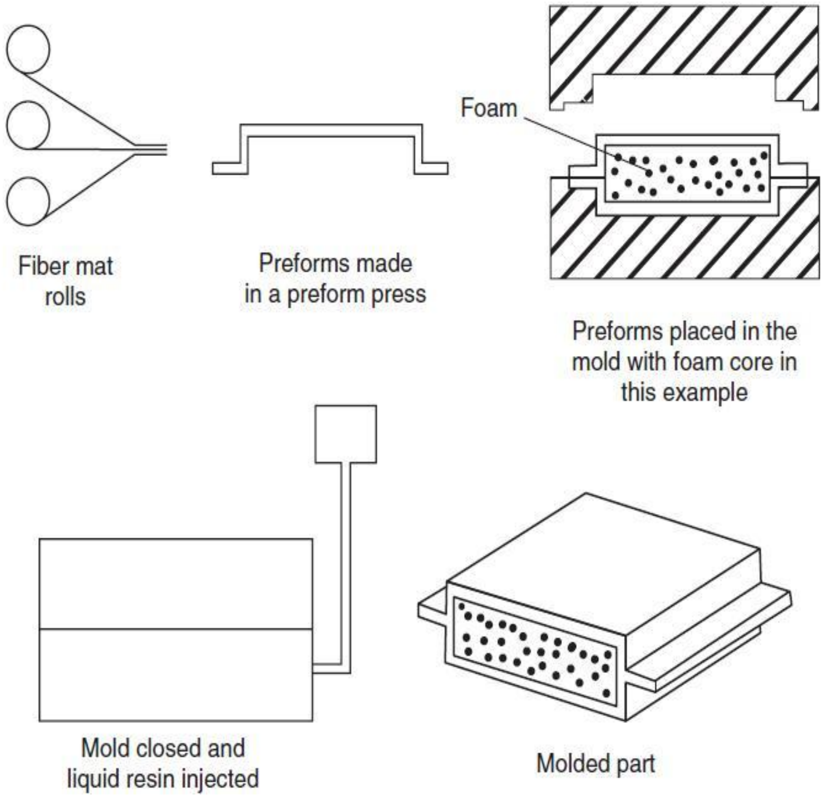


Fig 1.9 RTM process [4]

The curing is done at room temperature or at an elevated temperature, depending on the type of resin–catalyst system used. The main advantages of RTM is its ability to fabricate complex shape easily, low tooling cost. The arrays of shape such as bench sera tanks, both walls etc. can be formed by this method.

Elastic Reservoir molding

This method is used to construct thin panel mold having simple geometry like bus roof panel, radar reflectors and automotive body panel’s. In this method, a foam is used which consist of flexible polyurethane and stores liquid resin. A sandwich of foam and dry contain strand, woven roving or cloth is made and is placed in a heated mold. The mold is them pressed with pressure ranging from 520 to 1030 kPa. Due to compression, liquid resin flows out of foam and wets the face layer. Consequently, a low density fiber reinforced skin is formed after curing. The advantages of this process include low cost tooling and better stiffness to weight ratio.

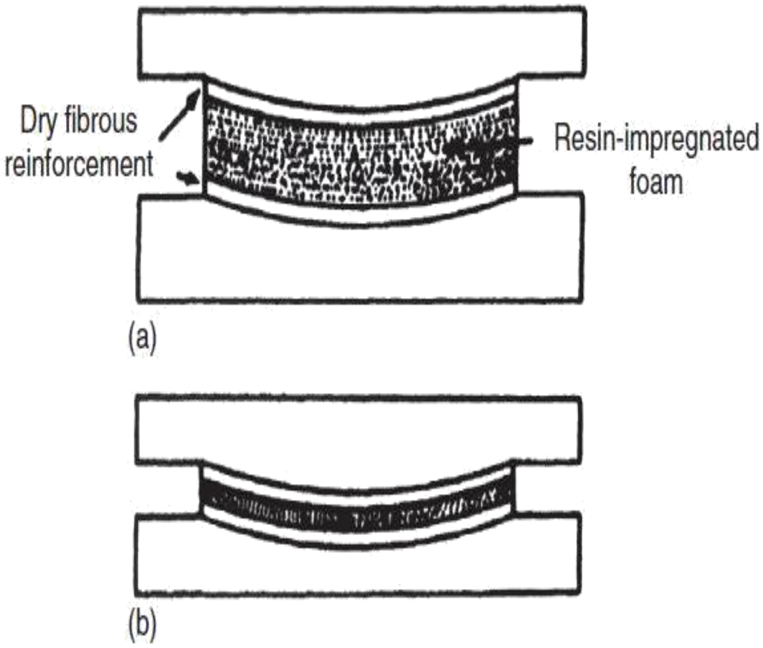


Fig 1.10 (a) and (b) Elastic reservoir molding [4]

Tube rolling

The method is used to make hollow circular tubes which are used in space trusses, bicycle frames etc. In this method precut prepeg are rolled onto the mandrel to form a hollow tube. After this, a heat shrinkable film is wrapped around and is cured in an air circulating oven at an elevated temperature. As a result, outer wrap shrinks tightly onto the rolled tube and entrapped air between the layers is squeezed out. The mandrel is removed at the end of this process and hollow tube is formed. The advantage of this process is faster production rate, low tooling cost and simple operation.

CHAPTER 2

Literature Survey

2.1 Literature reviews

This chapter includes the literature reviews on the studied paper related to this work.

Donnet et al. (1986) analysed the effect of plasma treatment on the mechanical properties of T300 carbon fibers for (2-30 min.) and observed that the tensile breaking load of CFs was decreased by 8%. The increased amount of oxygen content on CFs, existence of polar components and augmented etching with deeper grooves were observed on fiber.

Wu et al. (1995) observed the effect of oxidation on carbon fibers (CF) submerged in the nitric acid at 115°C for (20 - 90 minutes). The acidic capacities of CFs rose linearly and the tensile strengths of the fiber decreased with an increase in oxidation time. It was revealed that the surfaces of fibers were potholed and teared. In result the surface area of CFs after oxidation was generously proportioned than that of the untreated carbon fibers.

Su et al. (2005) described the effect of wet oxidation on the mechanical properties and surface morphology of the CFs. Carbon fibers were submerged in a 13 mol/L HNO_3 solution for 2h. The functional groups fashioned during the oxidation process, braced the bonding strength between the fabric and the resin. The XPS analytical results showed that the nitric acid treatment of the carbon fiber decreased the carbon concentration and increased the oxygen concentration on fabric. At the same time, the nitrogen concentration of the fabric significantly decreased by etching with HNO_3.

Xu et al. (2007) used the oxidation–reduction and pre-irradiation induced techniques to investigate the effect of acrylic acid on the wet ability of carbon fiber (CF) and the interfacial properties of CF/ epoxy. The surface of treated fiber was pragmatic rougher as compared to the neat carbon fiber. The tensile strength of the treated carbon fiber was improved by pre-irradiation process. The ILSS value of composites was enhanced as the bonding between fiber and epoxy of fiber became stronger.

Zhang et al (2007) analysed the effect of oxidation on topological behaviour of carbon fiber / polyamide composite. It was observed that increase in carbon content decreased the value of coefficient of friction and improved the wear resistance of the composites. It was assumed that time of running in period of neat PI was longer that of carbon fiber RPI composite and friction curve was more unsteadiness, resulting pitiable wear resistance under higher load. HNO_3 treatment increased the function groups which improve the bonding between fiber and matrix.

Zhang et al (2009) investigated the effect of oxidation on PAN based CFs.The surface of the fiber became rougher as compared with the virgin carbon fiber when treated with strong HNO_3 (90°C) for 1.5 hour. The oxygen concentration increased after surface treatment, which enhanced the linkage between the fiber and the PI matrix. After HNO3 oxidation process, there were additional functional groups (–O–C–,–C=O,–O–C=O) on the surfaces, which improved the total surface energy and polarity. It enhanced the wettability of the CFs with the matrix.

Li and Sun (2009) investigated the effect of nitric acid treatment on the surface of CFRP. Maleic anhydride graphted polystrene (MAH-g-polystrene) was added to the matrix and it was observed that contact angle was decreased. Lower the value of contact angle, the higher the linkage between carbon fabric and matrix. Photo electron spectra analysis showed strengthening of O-signals leading to rise in overall surface energy of the fibers .Interfacial shear strength was improved by MAH-g -Polythene modified resin

Song et al (2010) studied the effect of the surface roughness on the interfacial properties of carbon fibers. The surface of the fiber was treated with ammonia solution. The aqueous ammonia amplified the surface roughness while chemical composition of fiber remains unaffected. The treated fibers had superior wet ability on the surface, the surface energy was increased and the contact angle decreased against the solvents. The ILSS value was increased with increase in the treating time.

Liu et al. (2010) analyzed the effect of electrochemical oxidation on carbon fibers in $(NH_4HCO_3)/(NH_4)_2C_2O_4 \cdot H_2O$ aqueous compound solution. There was enhancement in interlaminar shear strength as the surface roughness increased, also caused by the combined effect of the oxygen containing and nitrogen containing functional groups on the carbon fibers. The electrochemical treatments made the surface of treated carbon fiber rougher than the untreated carbon fiber. The tensile strength of the carbon fiber increased by 17.1% and the ILSS augmented with the value of 14.5%.

Khan et al. (2010) investigated the effect of nanoclay addition on cyclic fatigue behaviour and residual properties of carbon fiber reinforced composites (CFRPs). The insertion of nanoclay into CFRPs composites enhanced the mechanical properties of the composites in static loading, also the fatigue life of the composites for the desired cyclic load level. The fatigue damaged area on the surface of the fiber was reduced with the assimilation of nanoclay. The flexural strength slightly reduced due to the lack of scattering at high clay content. The bonding between fiber-matrix was enhanced and nanoclay induced dimples were responsible for toughening mechanisms conscientious for the enhanced fatigue life of clay-CFRPs composites.

Tiwari et al. (2011) studied the effect of treatment of nitric acid on the surface of carbon fabric. It was concluded that with increase in treatment time (0-180 min.) surface roughnes was increased and tensile strength was lowered. ILSS and flexural strength were at maximum value for 90 min treatment. FTIR analysis showed that supplementary functional groups were attached to the treated fabric (ether, carbonyl and carboxyl) as compared with the virgin fiber. The wear of the composite was also reduced.

Zhang et al. (2011) analysed the effect of molecular weight of the sizing agent on surface of carbon fiber. The sizing agent with three altered molecular weights as S1 (Epoxy 601 with equivalent weight, 0.2), S2 (Epoxy 6101 with equivalent weight, 0.44) and S3 (Epoxy 618 with equivalent weight, 0.51) were used. The sizing on carbon fiber enhanced the handle ability of the carbon fiber in various processes and also protected the carbon fiber from oxidation and other impurities. The effect of S2 sizing agent on ILSS and ageing resistant property was more established than the S1 and S3.

Daia et al. (2011) investigated the effect of sizing on carbon fiber surface properties and fiber/epoxy interfacial adhesion by comparing sized and desized T300B with T700SC carbon fibers. The surface morphology analysis revealed that the concentration of activated carbon was fewer in desized carbon fiber. Inverse gas chromatography analysis showed that the dispersive surface energy of desized carbon fiber was privileged than the sized fiber. The IFSS value of the T300B and T700SC was lower than those of the desized carbon fiber. The acid parameters of carbon fibers surface reduced with sizing removal, which endorse the bonding strength at fiber/epoxy interface.

Tiwari et al. (2011) analyzed the effect of oxidation on the mechanical properties of the carbon fiber reinforced composites. The carbon fibers were treated with nitric acid (HNO_3, 65-68%) at 110°C duration varied from 15 to 180 minutes. In observation, with increased treatment time, roughness of fiber surface increased.

Wong et al. (2012) studied the effect of polypropylene (PP) composites reinforced fiber with recycled carbon fiber using extrusion compounding and injection molding. The improvement in reinforced potential of recycled fiber was observed as the interfacial adhesion between fiber and PP matrix was enhanced. The strength was increased with increase in the molecular weight of MAPP coupling agent. Due to superior compatibility between fiber and matrix, the composite impact strength was improved by MAPP. The tensile and flexural properties of composite were enhanced than unreinforced Polypropylene (PP).

Shi et al. (2012) analyzed that the tensile strength and flexural strength of the carbon fiber reinforced composite was improved by increasing the carbon fiber content (2-15%) in the matrix. It was also observed that the mechanical properties of the composite were enhanced by treating it with nitric acid, which further elevated when the carbon fiber was treated with silane coupling (KH 550) agent. FTIR analysis showed addition of functional groups on the surface of carbon fiber.

Yuan et al. (2012) studied the effect of oxidation and silanisation reaction on the carbon fabric. The tensile strength of the fabric was decreased with increase in the oxidation time (30-120 min).It was analyzed that tensile strength showed significant improvement after treated with APS at time interval of 60 min. SEM analysis proved that surface grooves had been deepened as the fiber was treated with nitric acid. The increased surface roughness and increased surface area improved the bonding between matrix and fibers.

Han et al. (2013) analyzed the effect of acid treatment (3:1 v/v mixture of concentrated H_2SO_4 / HNO_3 at 60°C) and neopentyl (diallyl) oxy, tri (dodecyl) pyro-phosphate titanate coupling agent on the interfacial properties of carbon fiber/epoxy composites. Acid treatment increased the surface roughness of carbon fiber. Fiber was treated for 3 hours with titanate coupling agent and was observed the tensile strength was reduced by 45.3%. The tensile strength was increased by 14.6%, when treated with 3 wt. % titanate coupling agent due to pore filling effect combined treatment fiber with acid and titanate coupling agent moderately reduced tensile strength because crevices were filled with coupling agent.

Jiang et al. (2015) analyzed the effect of surface treatment on the interfacial adhesion of CF composition. A combined treatment process was carried out (acetone desizing, nitric acid oxidation, $LiAlH_4$ reduction and silanisation reaction) in order to elevate the interfacial adhesion of CF composite. Results indicated that surface treatment improved wettability, polarity and toughness of CF surface without lowering the value of tensile strength of the CF.

Chapter 3

Research Problem

3.1 Gaps in literature:

From the review of literature, it is clear that a comparison of mechanical properties of carbon fiber reinforced composites by wet oxidation and silane treatment has not been reported.

The efficacy of wet oxidation, acetone desizing, wet oxidation followed by silane treatment of carbon fibers for improvement in mechanical properties of carbon fiber reinforced epoxy composites have not been studied.

3.2 Research problem:

Determine the mechanical properties of carbon fiber reinforced epoxy composites after surface treatments.

3.3 Objective of work:

- Study the effect of duration of wet oxidation on properties of carbon fibers and its composites.
- Compare the efficacy of commonly used surface treatment methods in improving interlaminar shear strength of composites.

Chapter 4

Fabrication and Experimentation

4.1 Fabrication of Samples:

4.1.1 Materials

Unidirectional carbon fibers were purchased from BASF. Araldite LY 1564 SP epoxy resin and Aradur 3486 BD hardener were procured from Huntsman India Limited. 3-Amino propyl triethoxy silane and 3-Glycidyloxy propyl trimethoxy silane were obtained from TCI chemicals, Chennai. Nitric acid (68% concentration) was procured from Adarsh chemicals, Chennai India. Acetone was obtained from Loba Chemie Pvt. Ltd. .

4.1.2 Surface treatment of carbon Fiber

The surface of the carbon fibers was modified by four different techniques in order to augment the mechanical properties of the carbon fibers reinforced composites:

a) The carbon fiber was treated with nitric acid (68% concentration). Fibers were engrossed and were permitted to remain in the aqueous solution of nitric acid for different time intervals (5min., 15min., and 30min.). Fibers were removed and washed with distilled water and then allowed to parch in the oven at 120^0C for 25 minutes.

b) Silanization of carbon fibers using APS: Amino silane was added to the acetone and stirred for 15 min. at 500rpm. pH of the solution was maintained between “4-5”.

   Fibers were immersed in the solution for different time intervals (5min, 15min and 30min.) and then were washed with acetone. Fibers were then permitted to desiccate in the oven at 110^0C for 15min. The fibers were also dried at room temperature.

c) Silanization of carbon fibers using GPS: The solvent was prepared by mixing ethanol and distilled water in ratio 90:10. Epoxy silane was added to the solvent slowly and stirred for 15 min at 500rpm. pH value of the solution was maintained by accumulation a mandatory amount of acetic acid to the solution. Fibers were immersed in the solution for 30min. and then the fibers were washed with ethanol. Fibers were then permitted to dry in the oven at 110^0C for 15min.

d) Wet oxidation followed by silane treatment: Fibers were treated with nitric acid as done in technique (a). Carbon fibers were then treated with amino silane. Acetone was poured into the beaker and was stirred at 500rpm for 10 min. Amino silane was then added to the acetone and stirred for 15 min. at 500rpm. pH of the solution was maintained between “4-5” by adding the obligatory amount of acetic acid to solution. Fibers were immersed in the solution for different time intervals (5min, 15min.) and then the Fibers were washed by acetone. Fibers were then allowed to arid in the oven at 110^{0}C for 15min.

Fig. 4.1 Vacuum Oven

[Courtesy: - CHED, TU, PTA.]

4.1.3 Manufacturing of carbon Fiber reinforced composites

Epoxy resin was mixed with the hardener in the recommended ratio 100:34 by weight. Hardener was slowly added to the resin while mechanical stirrer was used for uniform mixing of the epoxy with the hardener. Epoxy and hardener were allowed to swirl at 500rpm for 30min.

Fig. 4.2 Mechanical Stirrer

[Courtesy: - CHED, TU, PTA.]

Two plies of carbon fibers were laid on the flat surface of VARIM mould. A thick layer of epoxy resin was applied to fibers. Then peel ply, perforated film and infusion mesh were placed on it. Vacuum connections were made using breather cloth. Finally the vacuum bagging film was applied to seal the mould. The laminate was cured at 50ºC for 12 hours and then at room temperature for additional 12 hours.

Fig 4.3 Vacuum assisted resin infusion molding machine

[Courtesy: - CHED, TU, PTA.]

4.2 Specimens specifications

The specimens were primed and had been incise as per the ASTM standards D3039 and D790 for tensile and 3 point bending test correspondingly. The dimensions of specimens are revealed in the Table 4.1 below.

Table 4.1 Specimens specification for testing

Parameters	**Tensile Testing**	**Flexural Testing**
Length	250mm	50mm
Width	25.4mm	12.7mm
Thickness	$1_{-}^{+0}{}_{0.1}{}^{2}$	$1_{-}^{+0}{}_{0.1}{}^{2}$

4.3 Testing methods

4.3.1 Three point bending test

Three point bending test machine is revealed in Fig 4.4

Fig 4.4 Universal Testing Machine

[Courtesy: - CHED, TU, PTA.]

The specimens were notched according to the ASTM standard D790.

Rate of crosshead motion for machine was premeditated by:

$$R=ZL^2/6d \qquad \text{equation no.1}$$

Where

R= rate of crosshead motion,
mm/min. L= support span, mm
d= depth of beam, mm
Z= rate of straining of the outer Fiber, mm/mm/min. Z should be equal to 0.01
Specimens were test using Zwick/Roell universal testing machine.

4.3.2 Tensile testing

Carbon Fiber reinforced composite specimens were primed as per the ASTM standard D3039 to ordeal the tensile strength of the material on the universal testing machine. The specimens were tested until they allocate the break point. Load was applied at the rate 2mm per minute.

4.3.3 Scanning electron microscope

Scanning electron microscope revealed in Fig 4.5 was used to ordeal carbon Fiber reinforced composite specimens micro structures. The specimens were dimensioned as per the block size of the machine. Gold coating paraphernalia was used for polishing the specimens in order to augment the conductivity of the material shown in Fig 4.6. Micro structure of the refined specimens was experiential at 5µm and 10µm magnification. SEM micrographs endow with the information concerning the external morphology of the sample.

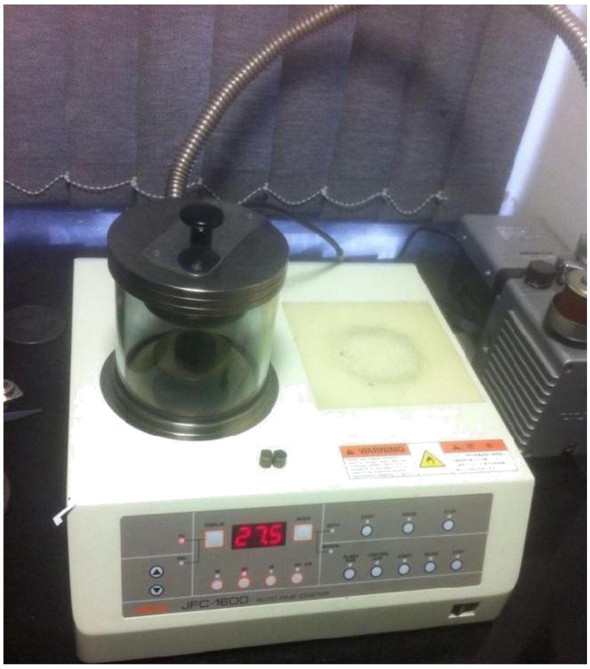


Fig. 4.5 SEM Machine **Fig. 4.6 Gold coating equipment**

[Courtesy: - SAI Labs, TU, PTA.]

4.3.4 Fourier Transform Infrared Spectroscopy

FTIR technique is a non-destructive technique which reveals information about the molecular structure of the sample shown in Fig 4.7. In this technique the infrared rays are conceded through the sample where some of the rays are absorbed and a number of are transmitted by the sample. The ensuing spectrum represents the molecular absorption and transmission, creating molecular fingerprints for the sample shown in Fig 4.8. FTIR analysis is used to investigate the unknown material. An infrared spectrum reveals the absorption peaks which directly relates to the frequencies of the vibration of the atomic bonds. The size of the peaks identifies the amount of material present in the particular sample.

Fig 4.7 FTIR machine [24]

Fig. 4.8 Block diagram of FTIR [25]

Chapter No. 5

Results and Discussions

5.1 Flexural Test

The results were obtained by performing three point flexural tests on the carbon fiber reinforced composites using Zwick/Roell universal testing machine are shown in table 5.1.

Table 5.1 Result for Flexural Test

Specimens Material	Specimens No.	Flexural Modulus (GPa)	Average Flexural Modulus (GPa)
NCF	1	2.16	1.96
	2	1.77	
	3	1.96	
ATCF	1	2.45	2.36
	2	2.40	
	3	2.25	
ESTCF	1	23.7	22.73
	2	20.0	
	3	24.5	
ASTCF	1	28.1	24.73
	2	24.8	
	3	21.3	
NA5ASTCF	1	22.6	25.23
	2	29.3	
	3	23.8	
NA15ASTCF	1	2.7	3.2
	2	2.5	
	3	2.2	
NA5TCF	1	2.1	2.1
	2	2.0	
	3	2.2	
NA15TCF	1	2.4	2.4
	2	2.5	
	3	2.3	
NA30TCF	1	19.3	19.63
	2	18.3	
	3	21.3	

Table 5.2 Results for Flexural Test

Specimens identifier	Specimens No.	Flexural strength (MPa)	Average flexural strength (MPa)
NCF	1	29	27.6
	2	26	
	3	28	
ATCF	1	51	41.66
	2	49	
	3	52	
ESTCF	1	283	307
	2	338	
	3	300	
ASTCF	1	432	373.33
	2	303	
	3	385	
NA5ASTCF	1	511	488.66
	2	495	
	3	460	
NA15ASTCF	1	58	56.33
	2	62	
	3	49	
NA5TCF	1	31	31.33
	2	28	
	3	35	
NA15TCF	1	46	43.33
	2	35	
	3	49	
NA30TCF	1	270	278.33
	2	277	
	3	288	

Surface treatment of the carbon fiber reinforced composite had resulted in improvement of flexural strength and flexural modulus.

5.2 Interlaminar shear strength:

The surface treatment of the carbon fiber reinforced composite had resulted in improvement of interlaminar shear strength, due to better bonding between the fiber and the matrix.

Table 5.3 Result of interlaminar shear strength

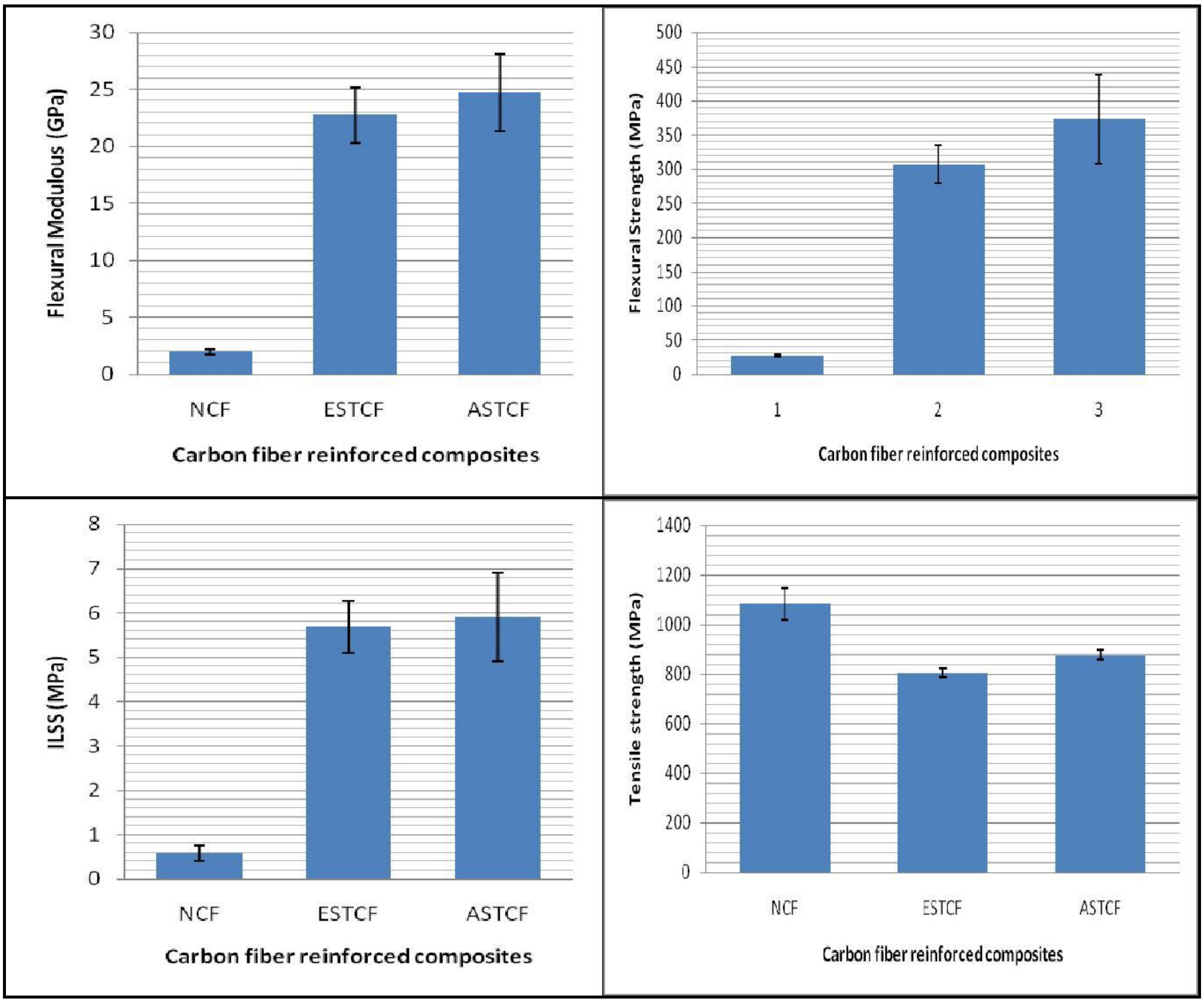
Specimens identifier	Specimens No.	Interlaminar shear strength (MPa)	Average interlaminar shear strength (MPa)
NCF	1	0.77	0.57
	2	0.44	
	3	0.52	
ATCF	1	0.93	0.94
	2	0.96	
	3	0.94	
ESTCF	1	5.24	5.68
	2	6.5	
	3	5.3	
ASTCF	1	7.05	5.90
	2	5.23	
	3	5.44	
NA5ASTCF	1	11.03	11.41
	2	11.55	
	3	11.66	
NA15ASTCF	1	1.4	1.30
	2	1.08	
	3	1.43	
NA5TCF	1	0.84	0.9
	2	1.04	
	3	0.82	
NA15TCF	1	1.09	1.05
	2	0.98	
	3	1.08	
NA30TCF	1	9.35	7.67
	2	6.86	
	3	6.8	

5.3 Tensile test:

The carbon fiber reinforced composite specimens were tested on Zwick/Roell universal testing machine and tensile results are reported below:

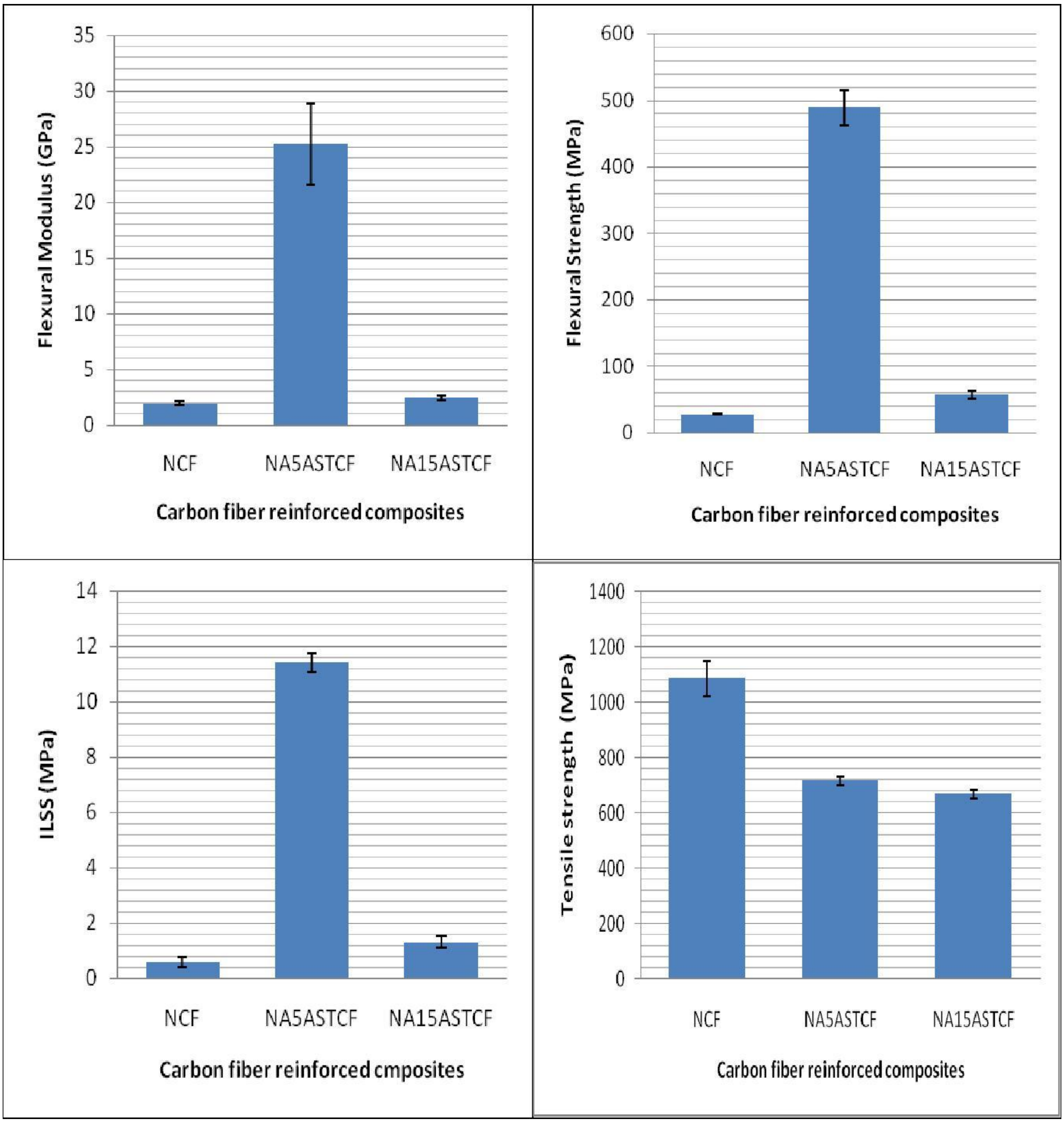
Table 5.4 Results of tensile strength test

S. No.	Specimens Indentifiers	Tensile strength (MPa)
1	NCF	1082.66
2	ATCF	863.60
3	ESTCF	804.40
4	ASTCF	877.77
5	NA5ASTCF	714.24
6	NA15ASTCF	666.07
7	NA5TCF	761.78
8	NA15TCF	732
9	NA30TCF	671.07



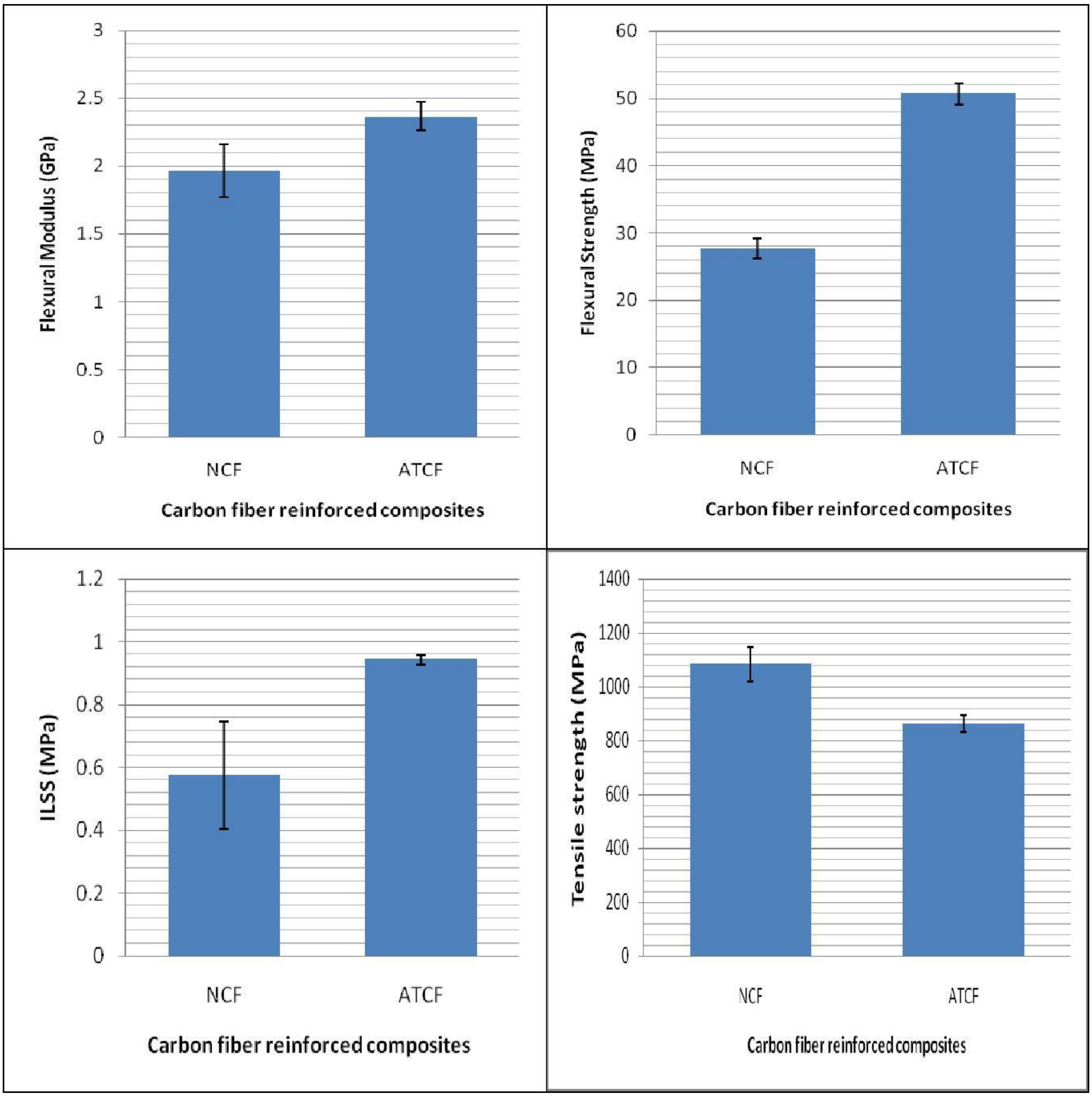
Graph 5.1 Effect of silane coupling agent on the mechanical properties of CFRP

Carbon fiber treated with silane coupling agent showed significant improvement in flexural strength, flexural modulus and interlaminar shear strength. However, the tensile strength decreased. Results indicate that 3-Aminopropy-triimethoxy silane is more efficient than 3-Glycidyloxypropyl-trimethoxy silane.



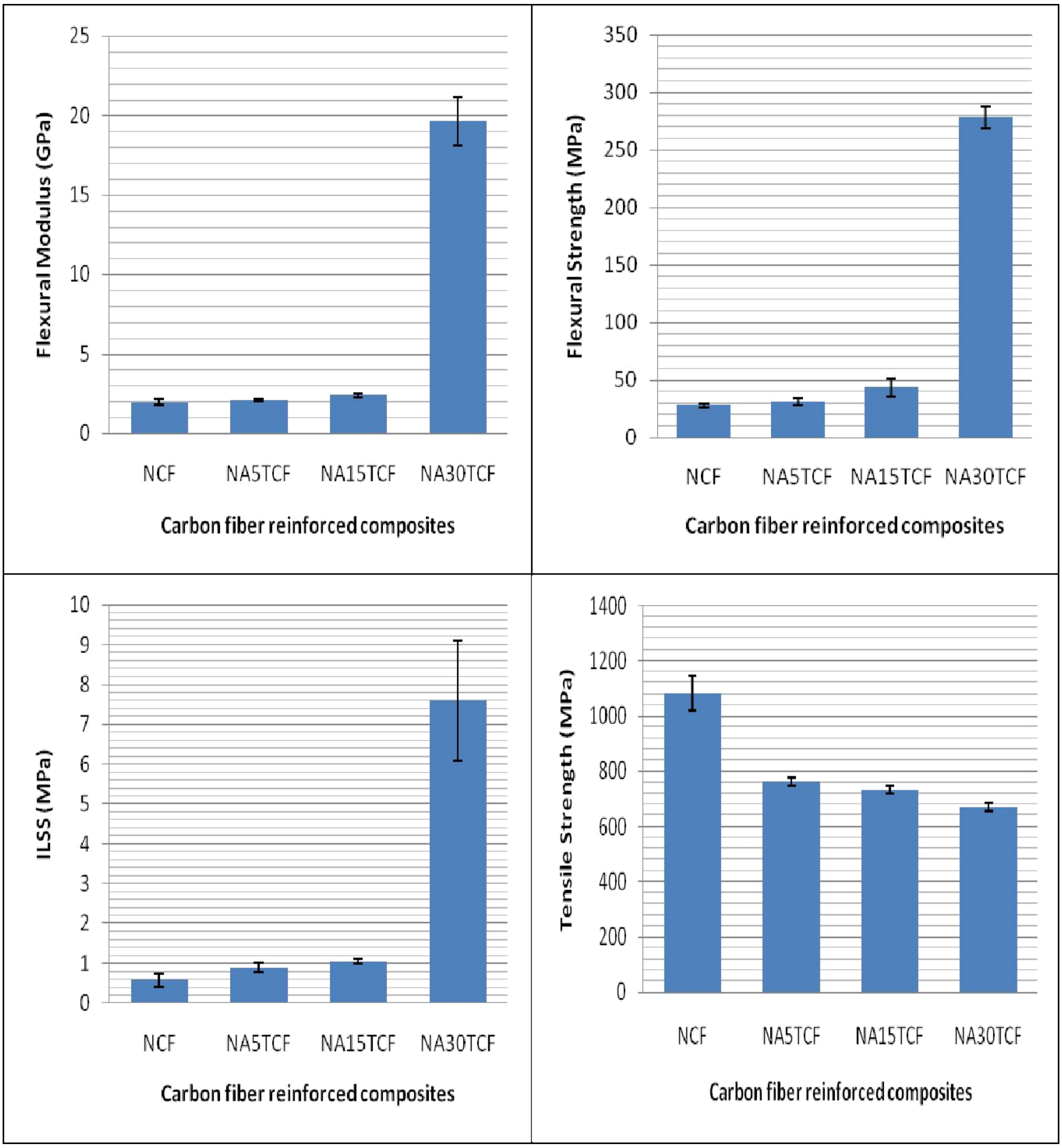
Graph 5.2 Effect of combined treatment of CF with nitric acid and amino silane

The treatment of CF with nitric acid followed silane coupling agent improved the flexural strength, flexural modulus and interlaminar shear strength. Maximum improvement is obtained when the fiber is treated with nitric acid for 5 minutes and then chemically modified by silane coupling agent.



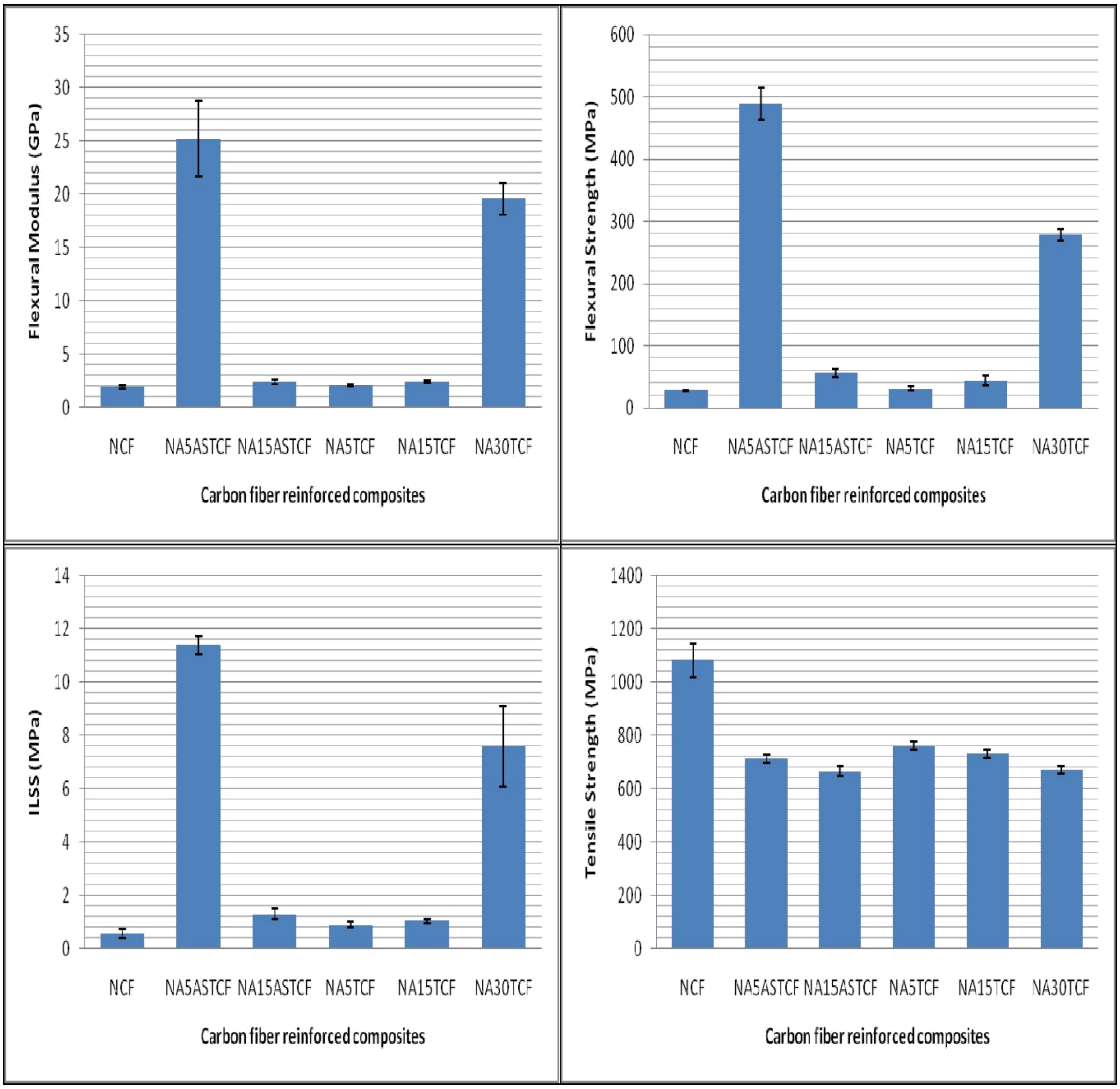
Graph 5.3 Effect of acetone desizing on CF

Acetone desizing has resulted in the improvement of mechanical properties (flexural strength, flexural modulus and interlaminar shear strength). However, there is reduction in the value of tensile strength



Graph 5.4 Effect of nitric acid on CF for different time intervals

Carbon fiber treated with nitric acid shows significant improvement in flexural strength, flexural modulus and interlaminar shear strength. When carbon fiber is treated with nitric acid for 30minutes, there is maximum improvement in mechanical properties. There is a reduction in the value of tensile strength due to the etching action of nitric acid.



Graph 5.5 Effect of nitric acid treatment and nitric acid followed by silane trearment on CF

The treatment of CF with nitric acid followed silane coupling agent and nitric acid improved the flexural strength, flexural modulus and interlaminar shear strength. Maximum improvement is obtained when the fiber is treated with nitric acid for 5 minutes and then chemically modified by silane coupling agent.

5.4 Scanning electron microscope (SEM)

Samples were fixed on the sample holder with the adhesive carbon tape. The samples were then plated with the gold in order to enhance the conductivity of the samples and trim down the reflection of radiations from the surface of the samples

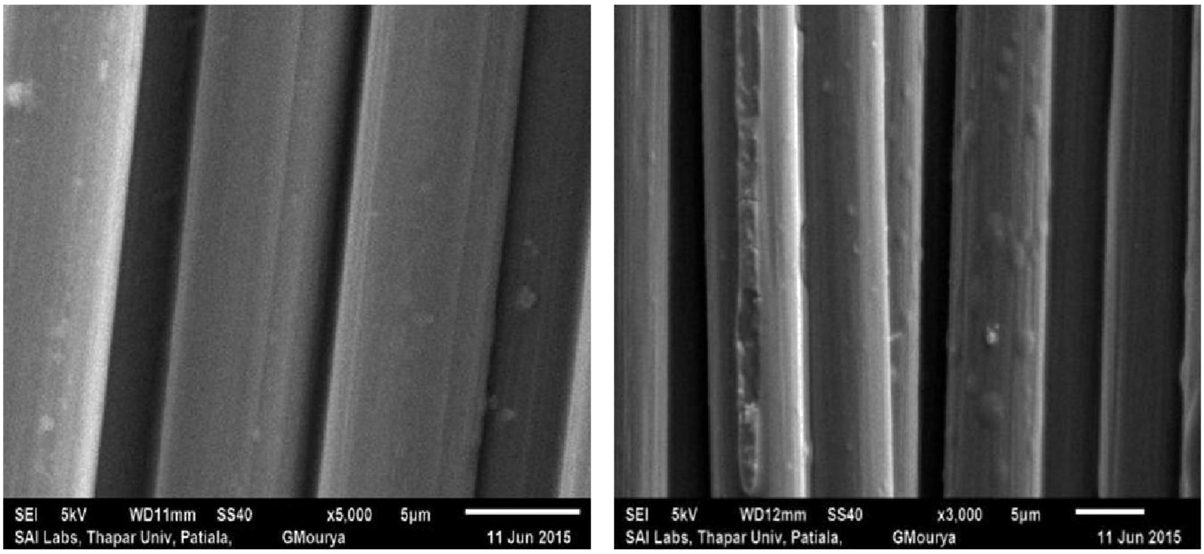
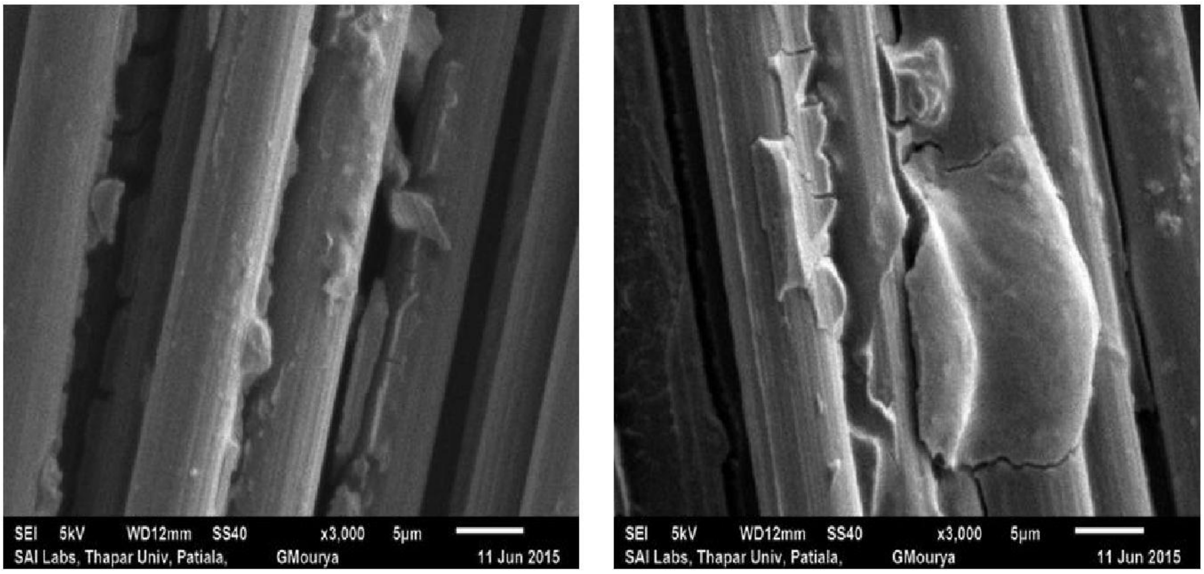


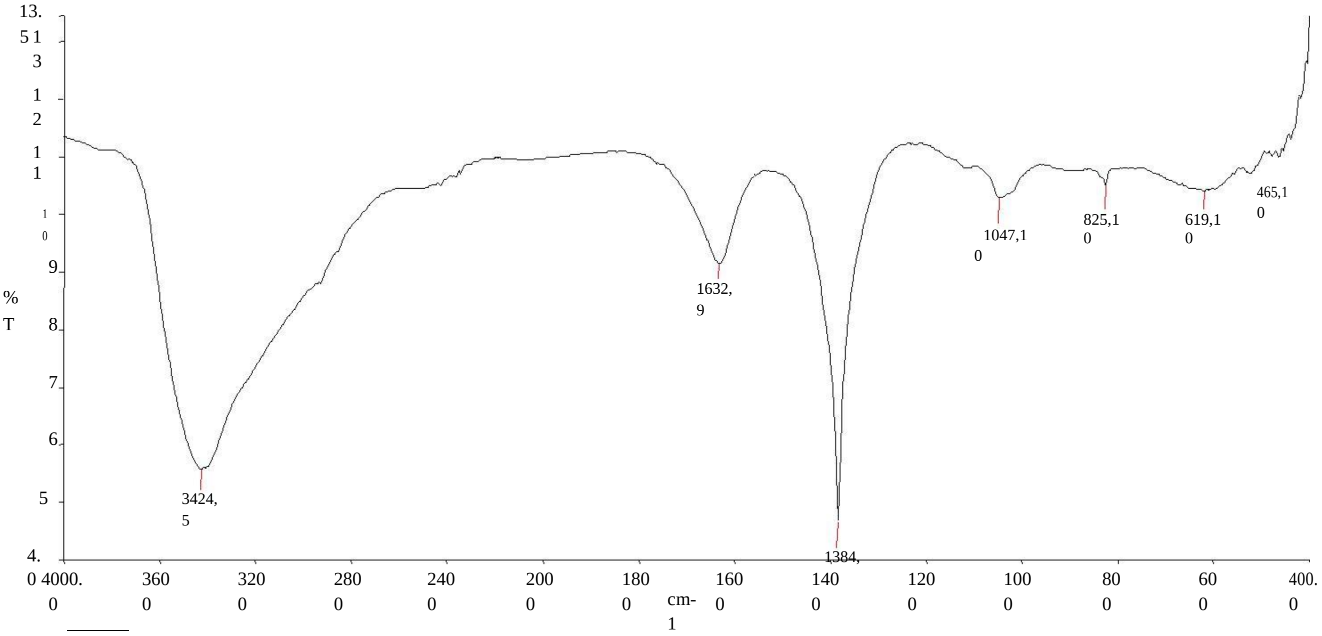
Fig 5.1 (a) SEM for untreated fiber **(b) SEM for treated fiber (5min.)**



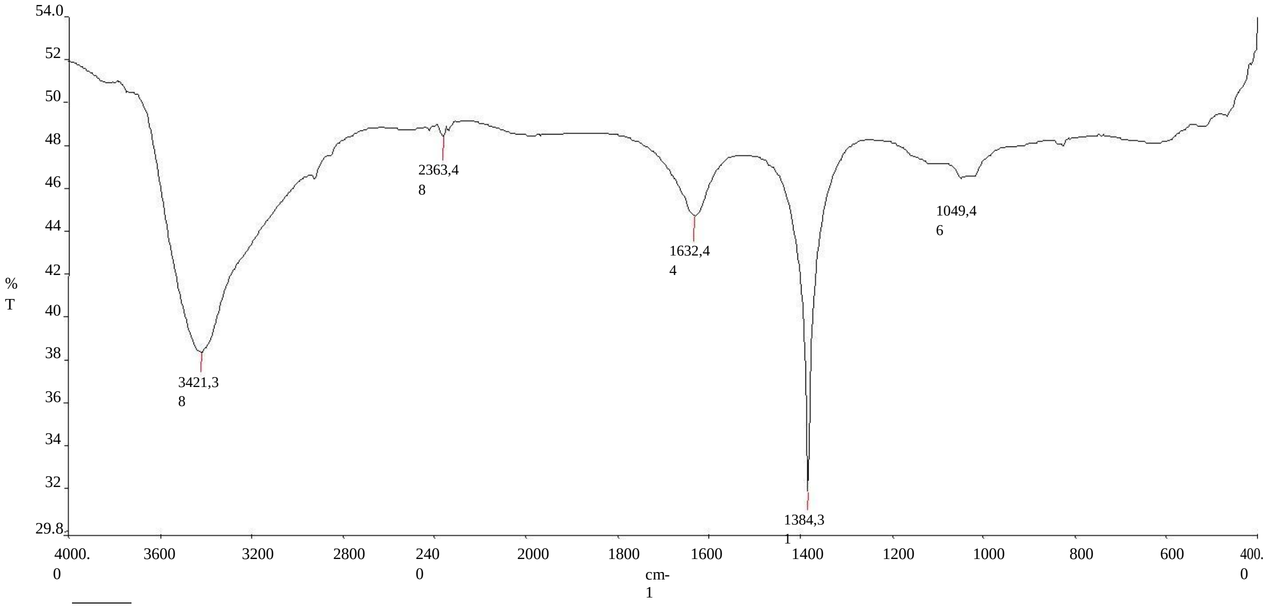
(c) SEM for treated fiber (15min.) **(d) SEM for treated fiber (30 min.)**

Fig 5.1 (a) revealed the structure of the virgin carbon fibers. It was analyzed that smooth fractured surfaces were formed. Fig (b), (c), (d) illustrates the effect of nitric acid on the surface of the carbon fiber. There appeared more protuberances and dongas on the surface of treated fiber. With increase in treatment time the surface of the carbon fiber became rougher and hence helps in better mechanical interlocking between the matrix and the resin which is also reported by (Donnet et al. [1] and Tiwari et al. [15]).

5.5 Fourier Transform infrared Reflectance spectroscopy (FTIR):



Graph 5.6 FTIR analysis



Graph 5.7 FTIR analysis

The peak in 950-1200 cm^{-1} range revealed the presence of ether type bands. The peak in the region 1350-1390 cm^{-1} is associated with C-N bands. The peak in range of 1500-1680 cm^{-1} is assigned to aromatic C=C and various substitute modes of aromatic rings. The peak in region

2300-2590cm^{-1} is allied to –C=N bands. The peak in range 3300-3500 cm^{-1} is interrelated to alcohol (OH) group. The data obtained from the above peak values reveals that the structure of the carbon fibers had changed. Active sites are created on the surface of the carbon fibers that enhance the bonding between fibers and matrix. There is an improvement in ILSS as a result of improvement in bonding between carbon fibers and the matrix is improved.

Chapter 6

Conclusion and Future scope

6.1 Conclusion

In this work the carbon fiber reinforced composites are manufactured by vacuum bagging process. The surface modifiers (conc.68% nitric acid, 3-Aminopropyl-trimethoxy silane, 3-Glycidyloxypropyl-trimethoxy silane, combined conc. 68% nitric acid and amino silane) resulted in the improvement of mechanical properties of carbon fiber reinforced composites (flexural strength, flexural modulus, interlaminar shear strength). Silane treatment of fibers imparted better mechanical properties to fiber reinforced composites in comparison to nitric acid treatment. Treating the fibers with nitric acid before silanization is useful because of two reasons. Firstly, it increases the surface area and secondly it creates –OH groups on fiber surface which improve the bond between inorganic part of silane and carbon fibers. Carbon fiber combined treated with nitric acid (5min.) and amino silane showed the best combination of properties. The apparent lower or no improvement in tensile strength of the treated carbon fiber reinforced composite can be attribute to the etching action of the surface modifier (conc. 68% nitric acid). The tensile strength of composites followed the order NCF>ASTCF> ATCF>ESTCF>NA5TCF>NA15TCF>NA5ASTCF>NA30TCF>NA15ASTCF.

6.2 Future scope

- Wear the properties can also be ascertained.
- Experiments can be repeated by changing conc. and time duration of treatment of the surface modifiers.
- Experiments may be performed on laminates with epoxy matrix modified with different nanoclays.
- Zirconate coupling agents can be better substitute to silane coupling agents.

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