CHARACTERIZATION OF HYBRID FRP COMPOSITES WITH HYGROTHERMAL EXPOSURE UNDER VARIED AMBIENT CONDITIONS

A REPORT SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology
in
Metallurgical and Materials Engineering

By

GYANARANJAN MISHRA

CHAITANYA PRASAD BASKE

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING
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Under the Guidance of

Prof. U.K. MOHANTY

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National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that the thesis entitle, "**CHARACTERIZATION OF HYBRID FRP COMPOSITES WITH HYGROTHERMAL EXPOSURE UNDER VARIED AMBIENT CONDITIONS**" submitted by **Mr. GYANARANJAN MISHRA** in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the any Degree or Diploma.

DATE: **Dr.U.K.MOHANTY,** PROFESSOR

                                                          Dept. of Metallurgical and Materials Engineering
                                                          National Institute of Technology, Rourkela-769008

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N.I.T. ROURKELA   GYANARANJAN MISHRA
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CONTENTS

ABSTRACT

The present experimental study aims at assessing the effect of moisture and temperature on the mechanical properties of hybrid FRP composites. Samples of several Carbon-Glass-Epoxy hybrids were manufactured using hand layup method where the stacking of plies was alternate and the weight fraction of fibre and matrix was kept at 50%-50%. Specimens were cut from the fabricated laminate according to the ASTM D 2344-84(1989) standards. Some of these specimens were kept in the As-Cured condition so as to obtain the base properties. Rest specimens were then subjected to hygrothermal environment where the relative humidity was maintained at 95% and the temperature at 60^0C for 24,48,72,96,120 hours. These specimens were divided into groups of five. One group was subjected to cryogenic conditions at -40^0C for 2 hours and the other group was subjected to elevated temperature at 50^0C for 2 hours. These treated samples were then subjected to short beam shear test or 3 point bend test. The ILSS (shear strength) values were then compared with the base values of as cured specimen. Differential scanning calorimetry was done to find the Tg variation. Degradation of mechanical property was found to be most prominent is case of specimens subjected to elevated temperature (50^0C) after hygrothermal treatment. SEM analysis was done to ascertain the mode of failure.

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1.INTRODUCTION

A COMPOSITE MATERIAL [1] is a macroscopic combination of two or more distinct materials, having a recognizable interface between them. Composites are used not only for their structural properties, but also for electrical, thermal, tribological, and environmental applications. Given the vast range of materials that may be considered as composites and the broad range of uses for which composite materials may be designed, it is difficult to agree upon a single, simple, and useful definition. As a common practical definition, composite materials may be restricted to emphasize those materials that contain a continuous matrix constituent that binds together and provides form to an array of a stronger, stiffer reinforcement constituent. The resulting composite material has a balance of structural properties that is superior to either constituent material alone. Composites typically have a fiber or particle phase that is stiffer and stronger than the continuous matrix phase and serve as the principal load carrying members. The matrix keeps the fibers in a desired location and orientation, separating fibers from each other to avoid mutual abrasion during periodic straining of the composite. The matrix acts as a load transfer medium between fibers, and in less ideal cases where the loads are complex, the matrix may even have to bear loads transverse to the fiber axis. The matrix is more ductile than the fibers and thus acts as a source of composite toughness. The matrix also serves to protect the fibers from environmental damage before, during and after composite processing [2]. A hybrid composite is a FRP composite which has more than one fiber as a reinforcement phase embedded into a single or multiple matrix phases. Hybridization provides the designers with an added degree of freedom in manufacturing composites to achieve high specific stiffness, high specific strength, enhanced dimensional stability, energy absorption, increased failure strain, corrosive resistance as well as reduced cost during fabrication [3]. Composites made of a single reinforcing material system may not be suitable if it undergoes different loading conditions during the service life. Hybrid composites may be the best solution for such applications [4]. By combining two or more types of fibers, it is possible to club the advantages of both the fibers while simultaneously mitigating their less desirable qualities. Normally, one of the fibers in a hybrid composite is a high-modulus and high-cost fiber such as carbon, boron and the other is usually a low-modulus fiber such as E-

glass, Kevlar. The high-modulus fiber provides the stiffness and load bearing qualities, whereas the low-modulus fiber makes the composite more damage tolerant and keeps the material cost low. The mechanical properties of a hybrid composite can be varied by changing volume ratio and stacking sequence of different plies. High-modulus fibers such as carbon, boron are widely used in many aerospace applications because of their high specific modulus. However, the impact strength of composites made of such high-modulus fibers is generally lower than conventional steel alloys or glass reinforced composites. An effective method of improving the impact properties of high-modulus fiber composites is to add some percentage of low-modulus fibers like E-glass. Most composite materials experience time varying internal disturbance of moisture and temperature during their service life time which can cause swelling and plasticization of the resin, distortion of laminae, deterioration of fiber/resin bond etc. These effects are collectively known as hygrothermal degradation, may be reversible on drying out the laminate and returning it to its initial condition, or permanent [5]. Because of the high performance laminates and composites, especially in aerospace, the effect of moisture/temperature environment has become an important aspect of composite material behavior. In this work the behavior of glass/carbon hybrid composites when exposed to varying temperature and moisture conditions is described. This is expected to be sensitive to moisture and temperature as the coefficients of expansion of glass and carbon fiber are different and the properties of glass/epoxy interface is sensitive to moisture.

2. WHY WE HAVE TAKEN UP THIS WORK?

The basic reason for working on such a topic arises from the fact that composites are vulnerable to environmental degradation. A moist environment, coupled with high or low temperature conditions is extremely detrimental for composites. There have been several efforts made by researchers in the last few years to establish the much needed correlation between the mechanical properties of the material and the moist environment or similar hygrothermal conditions, subjected to thermal shocks, spikes, ambient & sub ambient temperatures. But most research has been on the mechanical aspects rather than the physical & chemical interface and how this brings in change in the internal mechanical properties and affects a variety of other morphological changes.

The focus of our research has been to understand the physical changes that take place at the bonding interface between the fibers and the matrix, as it is of prime importance due to its link to the stress transfer, distribution of load, and it also governs the damage accumulation & propagation. This has wide significance in aerospace applications, because the aircraft components are exposed to harsh moist environment.

Hence our project work aims at the characterization of the hybrid FRP'S by DSC/SEM and to analyze the variation of Tg and flexural strength along with the mode of failure due to variation in moisture and temperature gradient.

3. LITERATURE REVIEW

3.1 <u>COMPOSITES</u>

A composite is combination of two materials in which one of the materials, called the reinforcing phase, is in the form of fibers, sheets, or particles, and is embedded in the other materials called the matrix phase. The reinforcing material and the matrix material can be metal, ceramic, or polymer. Composites are used because overall properties of the composites are superior to those of the individual components. For example: polymer/ceramic composites have a greater modulus than the polymer component, but aren't as brittle as ceramics. The following are some of the reasons why composites are selected for certain applications:

- High strength to weight ratio (low density high tensile strength)
- High creep resistance
- High tensile strength at elevated temperatures
- High toughness

Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile, or tough, material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The strength of the composite depends primarily on[5,6]:

- Fiber matrix ratio or hybridization
- Fiber orientation
- Stacking sequence

In some cases when strength along with ductility is required multiple reinforcements are used for example brittle carbon or aramid fibers (Kevlar29 and kevlar49) are incorporated into the matrix along with ductile glass fibers to create a "**hybrid composite**" which clubs the good properties while mitigating the less desirable properties of both.

Composites can be broadly classified into 3 categories:

- Particle-reinforced composites
- Fiber-reinforced composites
- Structural composites

3.2 FIBER-REINFORCED COMPOSITES

Reinforcing fibers can be made of metals, ceramics, glasses, or polymers that have been turned into graphite and known as carbon fibers. Fibers increase the modulus of the matrix material. The strong covalent bond along the fiber's length gives them a very high modulus in this direction because to break or extend the fiber the bonds must also be broken or moved. A high fiber aspect ratio (length: diameter ratio) permits very effective transfer of load via matrix materials to the fibers, thus taking advantage of there excellent properties. Therefore, fibers are very effective and attractive reinforcement materials.
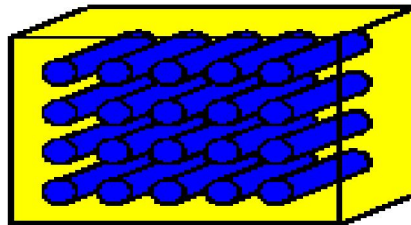
Fig. 3.1 showing a fiber reinforced composite

3.2.1 INFLUENCE OF FIBER LENGTH

The mechanical characteristics of a fiber reinforced composites depend not only on the properties of the fiber, but also on the degree to which an applied load is transmitted to the fibers by the matrix phase. Important to the extent of this load transmittance is the magnitude of the interfacial bond between the fiber and matrix phases. Some critical fiber length is necessary for effective strengthening and stiffening of the composite material. This critical length l_c is

dependent on the fiber diameter d and its ultimate (or tensile) strength σ_f^*, and on the fiber matrix bond strength (or shear yield strength of the matrix, whichever is smaller) τ_c according to

$$l_c = \sigma_f^* / 2 \tau_c$$

for a number of glass and carbon fiber –matrix combinations, this critical length is of the order of 1mm, which ranges between 20 and 150 times the fiber diameter. When a stress equal to σ_f^* is applied to a fiber having just this critical length maximum fiber load is achieved only at the axial center of the fiber. Fibers for which $l >> l_c$ (normally $l > 15l_c$) are termed continuous; discontinuous or short fibers have lengths shorter than this. For discontinuous fibers lengths significantly less than l_c, the matrix deforms around the fiber such that there is virtually no stress transference and little reinforcement by the fiber. To affect a significant improvement in strength of the composite, the fibers must be continuous.

3.2.2 INFLUENCE OF FIBER ORIENTATION [7]
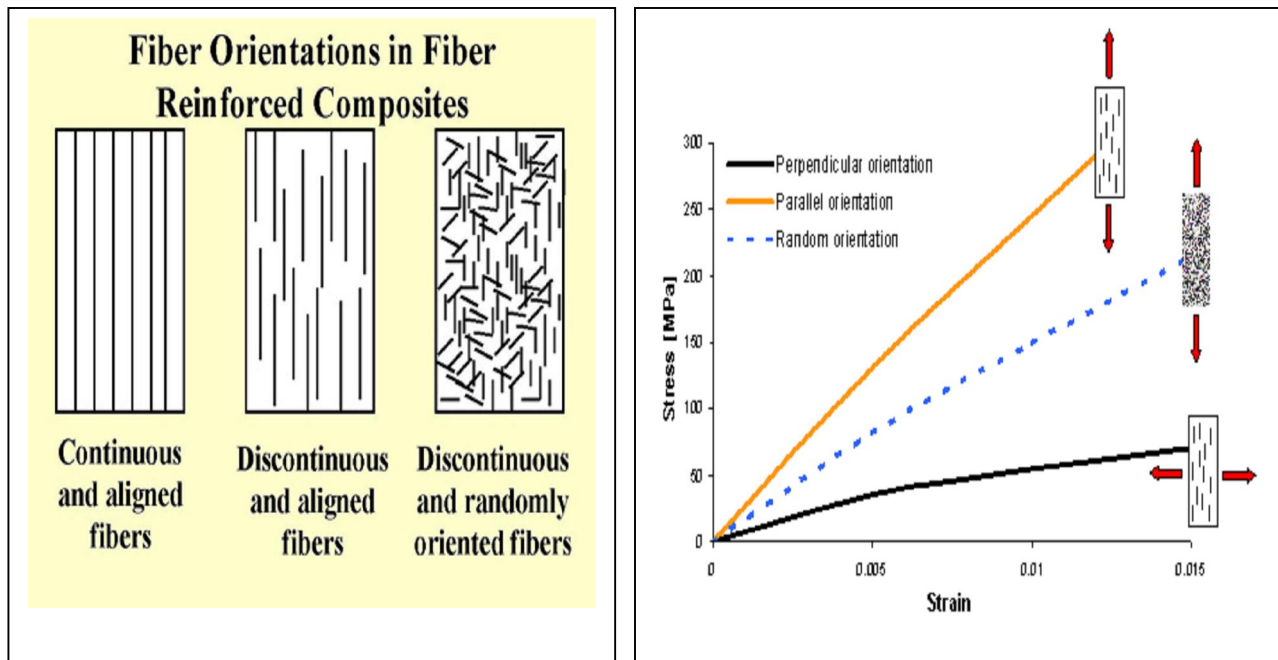
Fig.3.2 Effect of fiber orientation on strength of FRP composites

3.2.3 <u>MODULUS OF FIBER-REINFORCED COMPOSITES:</u>

Fibers have a very high modulus along their axis, but have a low modulus perpendicular to their axis. If the fibers are all parallel, the modulus of a fiber reinforced composite depends upon the direction of measurement. The modulus of the entire composite i.e. matrix plus reinforcement, is governed by the rule of mixtures when measuring along the length of the fiber:

$$E_c = E_f V_f + E_m V_m$$

E_c is the modulus of the entire composite along the length of the fiber.

E_f is the modulus of the fiber along the length of the fiber.

V_f is the volume percent occupied by the fibers.

E_m is the modulus of the matrix (usually not dependent upon direction)

V_m is the volume percent occupied by the matrix is equal to (1-Vf).

LONGITUDINAL LOADING

ISOSTRAIN CONDITION: Deformation of matrix and fibers is the same.

$$S_c = S_m * V_m + S_f * V_f$$

$$E_c = E_m * V_m + E_f * V_f$$

S = Tensile Strength
E = Modulus of Elasticity
V = Volume Fraction
m = Matrix
f = Fiber
c = Composite

Force parallel to fiber direction

TRANSVERSE LOADING

ISOSTRESS CONDITION: Matrix and fibers are under the same stress.$(S_c = S_m = S_f)$

$$E_c = \frac{E_m E_f}{V_m E_f + V_f E_m}$$

S = Tensile Strength
E = Modulus of Elasticity
V = Volume Fraction
m = Matrix
f = Fiber
c = Composite

Force perpendicular to fiber direction

Fig.3.3 Comparison of Loading type on Strength of Modulus of Elasticity

In case of hybrid composite the strength and modulus are governed by the law of hybrid mixture, given as [8]:

$$E = E_C V_C + E_G V_G + E_M V_M$$

E, V are the elastic modulus and volume fraction of components and the C, G and M are for carbon fiber, glass fiber and the matrix material.

3.3 TYPES OF FIBERS USED IN FIBER REINFORCED COMPOSITES:

- Glass fibers
- Carbon fibers
- Aramid fibers

3.3.1 GLASS FIBERS [9]

The most common reinforcement for the polymer matrix composites is a glass fiber. Most of the fibers are based on silica (SiO2), with addition of oxides of Ca, B, Na, Fe, and Al. The glass fibers are divided into different classes -- E-glass, S-glass and C-glass, M-glass, A-glass, D-glass. The E-glass is designated for electrical use and the S-glass for high strength. The C-glass is for high corrosion resistance, and it is uncommon for civil engineering application. M-glass has a high stiffness and A-glass commonly known for high alkali content and D-glass known for high di-electric property and commonly used for electrical applications. Of the all fibers, the E-glass is the most common reinforcement material used in civil structures. It is produced from lime-aluminaborosilicate which can be easily obtained from abundance of raw materials like sand. The glass fiber strength and modulus can degrade with increasing temperature. Although the glass material creeps under a sustained load, it can be designed to perform satisfactorily. The fiber itself is regarded as an isotropic material and has a lower thermal expansion coefficient than that of steel.

Fiber	Log 3 forming temperature[a]		Liquidus temperature		Softening temperature		Annealing temperature		Straining temperature		Bulk density, annealed glass, g/cm³
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	
General-purpose fibers											
Boron-containing E-glass	1160–1196	2120–2185	1065–1077	1950–1970	830–860	1525–1580	657	1215	616	1140	2.54–2.55
Boron-free E-glass	1260	2300	1200	2190	916	1680	736	1355	691	1275	2.62
Special-purpose fibers											
ECR-glass	1213	2215	1159	2120	880	1615	728	1342	691	1275	2.66–2.68
D-glass	...	...	...	...	770	1420	...	...	475	885	2.16
S-glass	1565	2850	1500	2730	1056	1935	...	...	760	1400	2.48–2.49
Silica/quartz	>2300	>4170	1670	3038	...	...	...	...	...	...	2.15

Fiber	Coefficient of linear expansion,	Specific heat,	Dielectric constant at room temperature	Dielectric strength,	Volume resistivity at room temperature	Refractive index	Weight loss in 24 h in 10%	Tensile strength at 23 °C (73 °F)		Young's modulus		Filament elongation at break, %
	10^{-6}/°C	cal/g/°C	and 1 MHz	kV/cm	$\log_{10}$ (Ω cm)	(bulk)	H_2SO_4, %	MPa	ksi	GPa	10^6 psi	
General-purpose fibers												
Boron-containing E-glass	4.9–6.0	0.192	5.86–6.6	103	22.7–28.6	1.547	~41	3100–3800	450–551	76–78	11.0–11.3	4.5–4.9
Boron-free E-glass	6.0	...	7.0	102	28.1	1.560	~6	3100–3800	450–551	80–81	11.6–11.7	4.6
Special-purpose fibers												
ECR-glass	5.9	...	...	...	...	1.576	5	3100–3800	450–551	80–81	11.6–11.7	4.5–4.9
D-glass	3.1	0.175	3.56–3.62	...	...	1.47	...	2410	349	...	...	...
S-glass	2.9	0.176	4.53–4.6	130	...	1.523	...	4380–4590	635–666	88–91	12.8–13.2	5.4–5.8
Silica/quartz	0.54	...	3.78	...	...	1.4585	...	3400	493	69	10.0	5

Table 3.1 Physical and mechanical properties of commercial glass fibers.

Fiber	Ref	Composition, wt%												
		SiO_2	B_2O_3	Al_2O_3	CaO	MgO	ZnO	TiO_2	Zr_2O_3	Na_2O	K_2O	Li_2O	Fe_2O_3	F_2
General-purpose fibers														
Boron-containing E-glass	1, 2	52–56	4–6	12–15	21–23	0.4–4	...	0.2–0.5	...	0–1	Trace	...	0.2–0.4	0.2–0.7
Boron-free E-glass	7	59.0	...	12.1	22.6	3.4	...	1.5	...	0.9	...	...	0.2	...
	8	60.1	...	13.2	22.1	3.1	...	0.5	...	0.6	0.2	...	0.2	0.1
Special-purpose fibers														
ECR-glass	1, 2	58.2	...	11.6	21.7	2.0	2.9	2.5	...	1.0	0.2	...	0.1	Trace
D-glass	1, 2	74.5	22.0	0.3	0.5	...	...	...	...	1.0	<1.3	...	...	...
	2	55.7	26.5	13.7	2.8	1.0	...	...	...	0.1	0.1	0.1	...	...
S-, R-, and Te-glass	1, 2	60–65.5	...	23–25	0–9	6–11	...	...	0–1	0–0.1	...	...	0–0.1	...
Silica/quartz	1, 2	99.9999	...	...	...	...	...	...	...	...	...	...	...	...

Table 3.2 composition of commercial glass fibers

3.3.1.1 STRUCTURE OF GLASS FIBER

Glass fibers have high tensile strength, impact strengths and high chemical resistance. But these have relatively low modulus, self-abrasiveness, low fatigue resistance and poor adhesion to matrix composites.
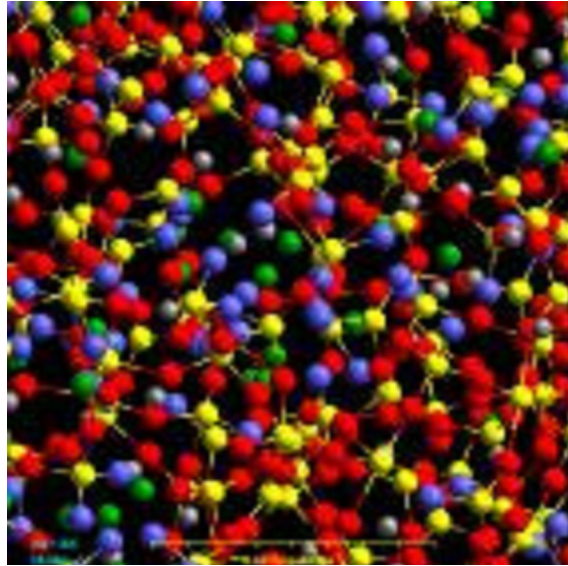
Fig 3.4 showing structure of glass fibers

The three dimensional network of structure of glass results in isotropic properties of glass fibers, in contrast to those of carbon and Kevlar aramid fibers which are anisotropic. The elastic modulus of glass fibers measured along the fiber axis is the same as that measured in the transverse direction, a characteristic unique to glass fibers.

3.3.1.2 SURFACE TREATMENT OF REINFORCING MATERIALS

Surface treatment is done to improve the adhesion of fillers and fibers to matrix resin by Modifying the surface of the solid. Often, chemical structure and sometimes topology of the surface change upon the treatment.

3.3.2 CARBON FIBERS

Carbon fiber is the most expensive of the more common reinforcements, but in space applications the combination of excellent performance characteristics coupled with light weight make it indispensable reinforcement with cost being of secondary importance. Carbon fibres consist of small crystallite of turbostratic graphite. These resemble graphite single crystals except that the layer planes are not packed in a regular fashion along the c-axis direction. In a graphite single crystal the carbon atoms in a basal plane are arranged in hexagonal arrays and held

together by strong covalent bonds. Between the basal planes only weak Van-der-waal forces exist. Therefore the single crystals are highly anisotropic with the plane moduli of the order of 100 Gpa whereas the molecules perpendicular to the basal plane are only about 75 GPa. It is thus evident that to produce high modulus and high strength fibers, the basal planes of the graphite must be parallel to the fiber axis. They have lower thermal expansion coefficients than both the glass and aramid fibers. The carbon fiber is an anisotropic material, and its transverse modulus is an order of magnitude less than its longitudinal modulus. The material has a very high fatigue and creep resistance. Since its tensile strength decreases with increasing modulus, its strain at rupture will also are much lower. Because of the material brittleness at higher modulus, it becomes critical in joint and connection details, which can have high stress concentrations. As a result of this phenomenon, carbon composite laminates are more effective with adhesive bonding that eliminates mechanical fasteners [10].

Typical Properties	Density (g/cm^3)	Young's Modulus (GPa)	Tensile Strength (GPa)	Tensile Elongation (%)
High Strength	1.8	230	2.48	1.1
High Modulus	1.9	370	1.79	0.5
Ultra-High Modulus	2.0 - 2.1	520 – 620	1.03 - 1.31	0.2

Table 3.3 typical properties of carbon fiber.

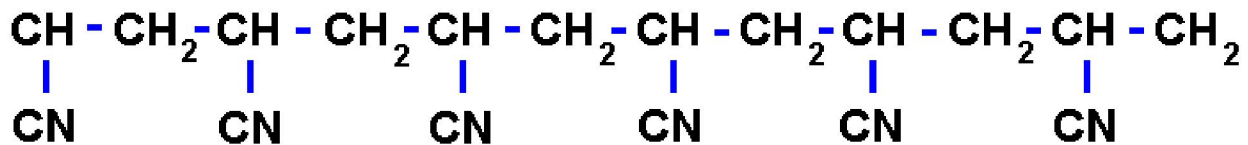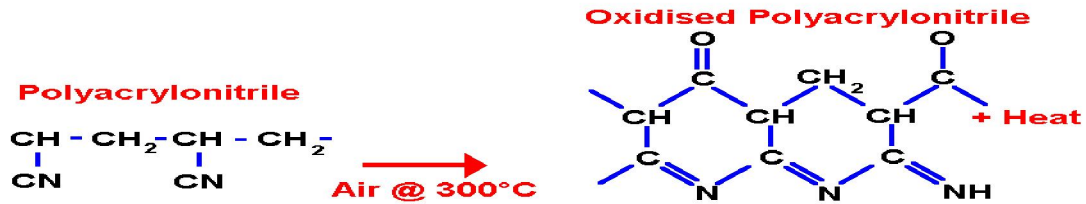The basic unit from where carbon fibers are produced is PAN

Fig. 3.5 showing the basic unit of PAN

The conversion of PAN to carbon fiber is done as shown below:

- OXIDATION involves heating the fibers to around 300 ºC in air. This evolves hydrogen from the fibers and adds less volatile oxygen

- CARBONIZATION OR GRAPHITISATION involving heating the fibers upto 3000^0C in an inert atmosphere to make the fiber 100% carbon
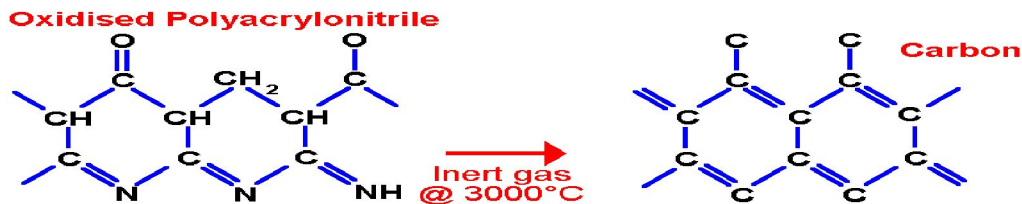
Carbon fibers are derived from one of two precursor materials

- PITCH
- PAN *(Polyacrilonitrile fibers)*

PITCH based carbon fibers have lower mechanical properties and are therefore rarely used in critical structural applications. PAN based carbon fibers are under continual development and are used in composites to make materials of great strength and lightness.

3.3.3 KEVLAR FIBERS

Kevlar (poly-paraphenylene terephthalamide) is the DuPont Company's brand name for a synthetic material constructed of para-aramid fibers that the company claims is five times stronger than the same weight of steel, while being lightweight, flexible and comfortable. It is

also very heat resistant and decomposes above 400 °C without melting. Kevlar is a registered trademark of E.I. du Pont de Nemours and Company [11].

Originally intended to replace the steel belts in tires, it is probably the most well known name in soft armor (bulletproof vests). It is also used in extreme sports equipment, high-tension drumhead applications, animal handling protection, composite aircraft construction, fire suits, yacht sails, and as an asbestos replacement. When this polymer is spun in the same way that a spider spins a web, the resulting commercial para-aramid fiber has tremendous strength, and is heat and cut resistant. Para-aramid fibers do not rust or corrode, and their strength is unaffected by immersion in water. When woven together, they form a good material for mooring lines and other Underwater objects. However, unless specially waterproofed, para-aramid fibre's ability to stop bullets and other projectiles is degraded when wet. Kevlar is a type of aramid that consists of long polymeric chains with a parallel orientation. Kevlar derives its strength from intermolecular hydrogen bonds and aromatic stacking interactions between aromatic groups in neighboring strands. These interactions are much stronger than the Van der Waals interaction found in other synthetic polymers. The presence of salts and certain other impurities, especially calcium, would interfere with the strand interactions and has to be avoided in the production process. Kevlar consists of relatively rigid molecules, which form a planar sheet-like structure similar to silk protein.
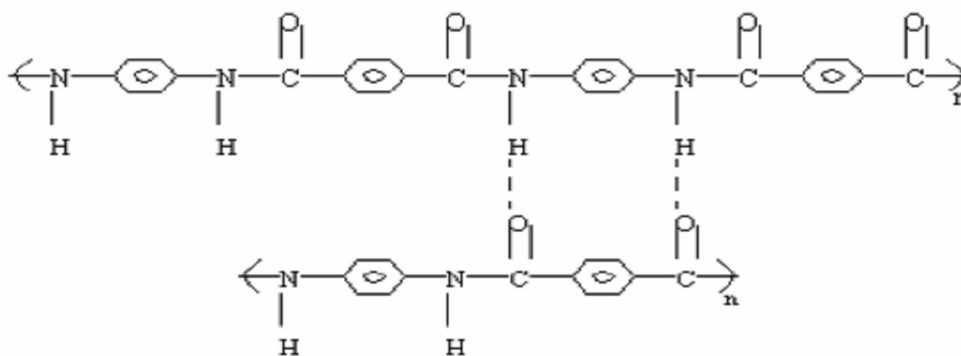

Fig.3.6 showing the basic unit of aramid fiber

These properties result in its high mechanical strength and its remarkable heat resistance. Because it is highly unsaturated, i.e. the ratio of carbon to hydrogen atoms is quite high, it has a low flammability. Kevlar molecules have polar groups accessible for hydrogen bonding. Water

that enters the interior of the fiber can take the place of bonding between molecules and reduce the material's strength, while the available groups at the surface lead to good wetting properties. This is important for bonding the fibers to other types of polymer, forming a fiber reinforced plastic. This same property also makes the fibers feel more natural and "sticky" compared to non-polar polymers like polyethylene. In structural applications, Kevlar fibers can be bonded to one another or to other materials to form a composite. Kevlar's main weaknesses are that it decomposes under alkaline conditions or when exposed to chlorine. While it can have a great tensile strength, sometimes in excess of 4.0 GPa, like all fibers it tends to buckle in compression.
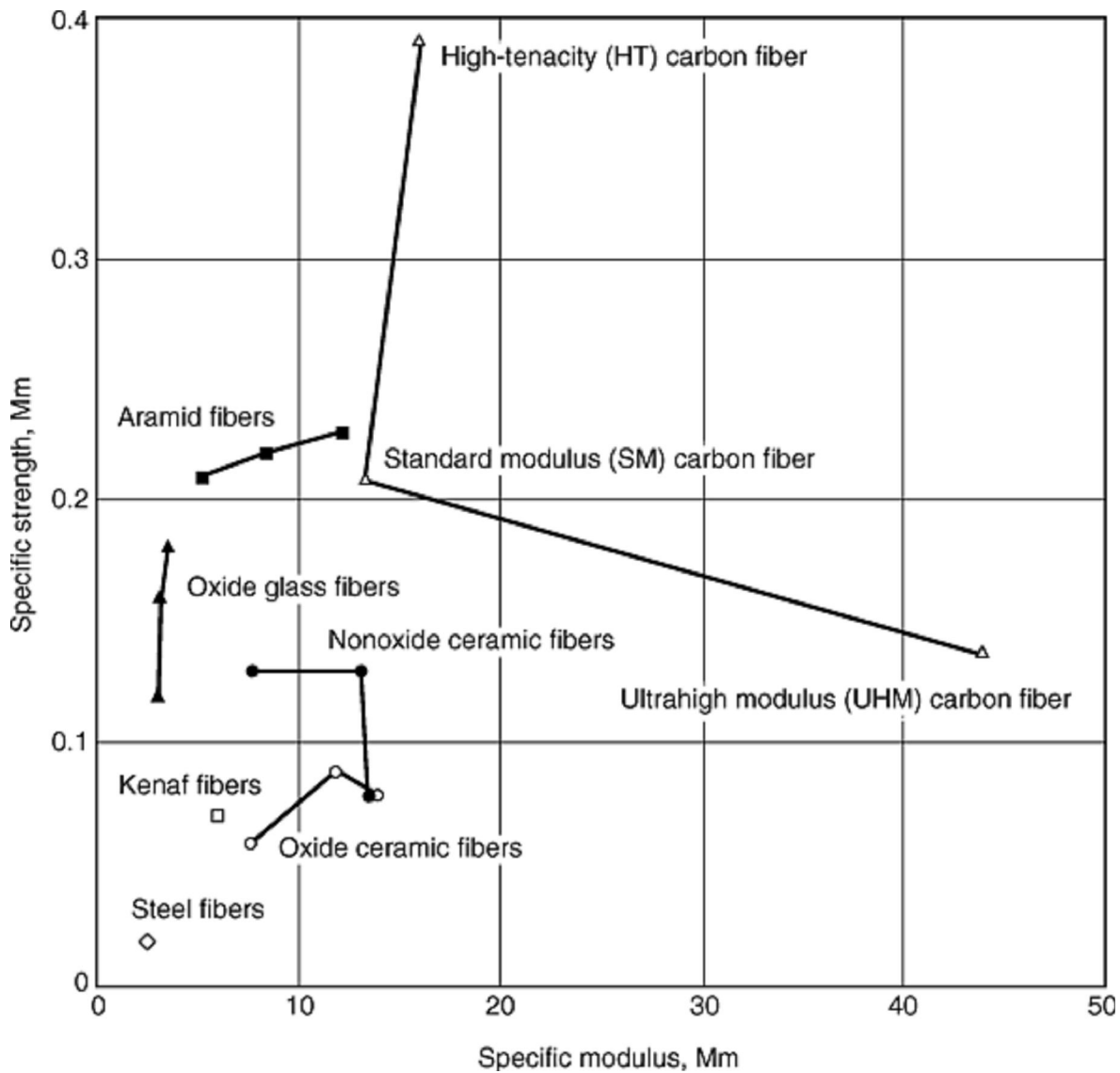

Fig. 3.7 Specific properties of selected reinforcing fibers [12]

3.4 <u>MATRIX PHASE INA FRP COMPOSITE</u>

Fibers, since they cannot transmit loads from one to another, have limited use in engineering applications. When they are embedded in a matrix material, to form a composite, the matrix serves to bind the fibers together, transfer loads to the fibers, and damage due to handling. The matrix has a strong influence on several mechanical properties of the composite such as transverse modulus and strength, shear properties, and properties in compression. Physical and chemical characteristics of the matrix such as melting or curing temperature, viscosity, and reactivity with fibers influence the choice of fabrication process. The matrix material for a composite system is selected, keeping in view all these factors. The most commonly used matrix material is described below:

3.4.1 <u>EPOXY RESIN</u>

Epoxy resins are relatively low molecular weight pre-polymers capable of being processed under a variety of conditions. Two important advantages of these resins are over unsaturated polyester resins are: first, they can be partially cured and stored in that state, and second they exhibit low shrinkage during cure. However, the viscosity of conventional epoxy resins is higher and they are more expensive compared to polyester resins. The cured resins have high chemical, corrosion resistance, good mechanical and thermal properties, outstanding adhesion to a variety of substrates, and good and electrical properties. Approximately 45% of the total amount of epoxy resins produced is used in protective coatings while the remaining is used in structural applications such as laminates and composites, tooling, moulding, casting, construction, adhesives, etc [13].

Epoxy resins are characterized by the presence of a three-membered ring containing two carbons and an oxygen (epoxy group or epoxide or oxirane ring). Epoxy is the first liquid reaction product of bisphenol-A with excess of epichlorohidrin and this resin is known as diglycidylether of bisphenol A (DGEBA). DGEBA is used extensively in industry due to its high fluidity, processing ease, and good physical properties of the cured of resin.
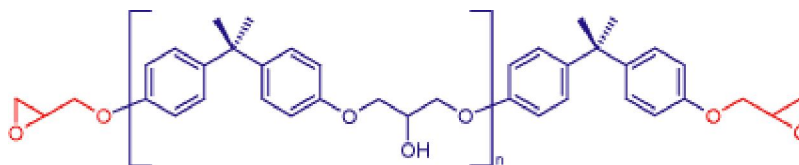
Fig 3.8 Showing structure of DGEBA

A range of epoxy resins is now available, varying from relatively tough low temperature epoxies for use in construction industry to brittle epoxies for use in construction industry to brittle epoxies useful in aerospace sector. This widespread application of epoxy resin is primarily due to the availability of resins with different backbone structures and molecular weights to give products with low viscosity (liquids) to low melting point solids. The ease of processing, good melting characteristics, excellent adhesion to various types of substrates, low shrinkage during cure, superior mechanical properties of cured resin, and good thermal and chemical resistance have made epoxy resin a material of choice in advanced fiber reinforced composites.

Ethylene diamines are most widely used aliphatic amines for cured epoxy resins. These are highly reactive, low molecular weight curing agents that result in tightly cross-linked network. One primary amino group reacts with two epoxy groups. The primary and secondary amines are reactive curing agents. The primary amino group is more reactive towards epoxy than secondary amino groups are consumed (95%), whereas only 28% of secondary amino groups are consumed.
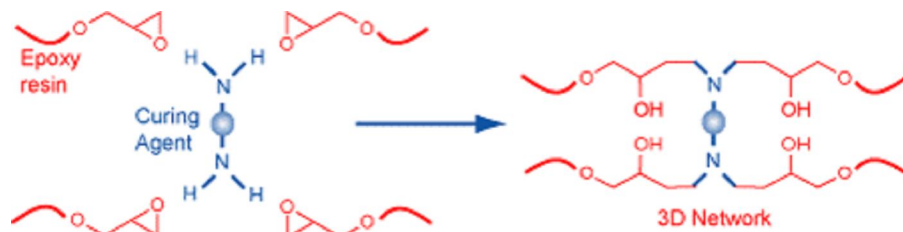
Fig 3.9 showing the curing of epoxy resin with primary amines

The primary amino-epoxy reaction results in linear polymerization while secondary amino-epoxy reaction leads to branching and cross-linking. The cured epoxy resins find a variety of applications as adhesives, laminates, sealants, coatings, etc. The optimum curing temperature and the thermal stability of epoxy resin depend on the type of curing agent. The anhydride cured epoxy resins have excellent electrical, chemical, and mechanical properties and are used for electrical and electronic applications. Epoxies are used as binders in materials for construction. Filling of cracks in concrete structures is achieved by epoxies. In construction industry, for bonding and coating purposes, low temperature curing of epoxies is achieved by using thiols that

exhibit higher curing rates. Epoxy based prepregs have been used in numerous aircraft components such as rudders, stabilizers, elevators, wing tips, launching gear doors, radomes, ailerons, etc. The composite materials constitute 3-9% of total structural weight of the commercial aircrafts such as Boeing 767 or Boeing 777. Composite and laminate industry uses 28% of epoxy resins produced. Besides these applications, the applications, the major user of epoxy is coating industry.

Resins	Density ρ (kg/m^3)	Elastic Modulus E(Mpa)	Shear Modulus G(Mpa)	Poisson Ratio v	Tensile Strength σ_{Ult} (Mpa)	Elongation E%	Coefficient of Thermal Expansion α(°C^{-1})	Coefficient of Thermal Conductivity λ(W/m°C)	Heat Capacity C(J/kg°C)	Useful Temperature Limit T_{max} (°C)	Price 1993 ($/kg)
					Thermosets						
Epoxy	1200	4500	1600	0.4	130	2 (100°C) 6 (200°C)	11×10^{-5}	0.2	1000	90 to 200	6 to 20
Phenolic	1300	3000	1100	0.4	70	2.5	1×10^{-5}	0.3	1000	120 to 200	
Polyester	1200	4000	1400	0.4	80	2.5	8×10^{-5}	0.2	1400	60 to 200	2.4
Polycarbonate	1200	2400		0.35	60		6×10^{-5}		1200	120	
Vinylester	1150	3300			75	4	5×10^{-5}			>100	4
Silicone	1100	2200		0.5	35					100 to 350	
Urethane	1100	700 to 7000			30	100				100	4
Polyimide	1400	4000 to 19,000	1100	0.35	70	1	8×10^{-5}	0.2	1000	250 to 300	
					Thermoplastics						
Polypropylene (pp)	900	1200		0.4	30	20 to 400	9×10^{-5}		330	70 to 140	
Polyphenylene sulfone (pps)	1300	4000			65	100	5×10^{-5}			130 to 250	
Polyamide (pa)	1100	2000		0.35	70	200	8×10^{-5}		1200	170	6
Polyether sulfone (pes)	1350	3000			85	60	6×10^{-5}			180	25
Polyetherimide (pei)	1250	3500			105	60	6×10^{-5}	0.2		200	20
Polyether-ether-ketone (peek)	1300	4000			90	50	5×10^{-5}	0.3		140 to 250	96

Table 3.4 showing typical properties of commonly used resins [14]

3.5 ADVANTAGES OF COMPOSITE MATERIALS OVER OTHER CONVENTIONAL MATERIALS

- Stronger and stiffer than metals on a density basis For the same strength, lighter than steel by 80% and aluminum by 60%. Hence Superior stiffness-to-weight ratios.
- Highly corrosion resistant:

Essentially inert in most corrosive environments. Benefits include lower maintenance and replacement costs.

- Tailor able thermal expansion properties

  Can be compounded to closely match surrounding structures to minimize thermal stresses

- Exceptional formability

  Composites can be formed into many complex shapes during fabrication, even providing finished, styled surfaces in the process.

- Low investment in fabrication equipment

  The inherent characteristics of composites typically allow production to be established for a small fraction of the cost that would be required in metallic fabrication.

- Good dimensional stability (extremely low coefficient of thermal expansion).

- Reduced Part Counts

  Parts that were formerly assembled out of several smaller metallic components can be fabricated into a larger single part. This reduces manufacturing and assembly labor and time.

3.6 <u>APPLICATIONS</u>

The composites industry has begun to recognize that the commercial applications of composites promise to offer much larger business opportunities than the aerospace sector due to the sheer size of transportation industry. Thus the shift of composite applications from aircraft to other commercial uses has become prominent in recent years [15]. Unlike conventional materials (e.g., steel), the properties of the composite material can be designed considering the structural aspects. The design of a structural component using composites involves both material and structural design. Composite properties (e.g. stiffness, thermal expansion etc.) can be varied continuously over a broad range of values under the control of the designer. Careful selection of reinforcement type enables finished product characteristics to be tailored to almost any specific engineering requirement.

Composites are used for the following purposes:
- Electrical and electronics

- Buildings and public works

- Road, rail, marine, cable, air, space transport

- General mechanical applications

- Sports and recreation

- Chemical, Oil and refinery industries
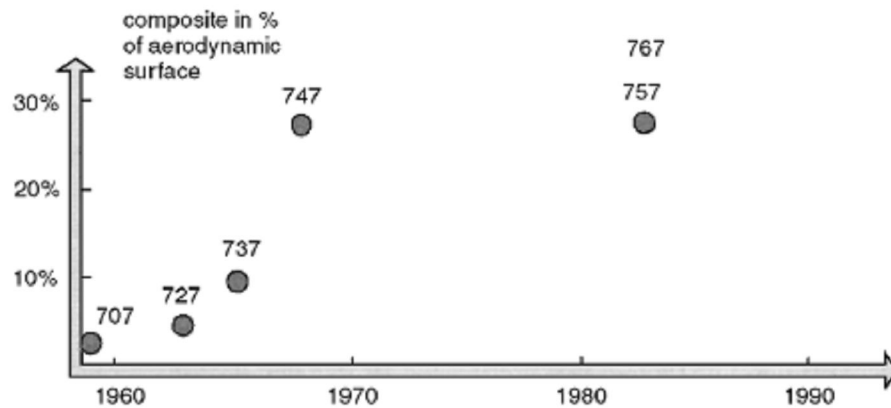
- Bio-mechanics applications

Fig 3.10 showing the amount of composite used in the Boeing aircraft [16] with passage of year

3.7 HYBRID FRP COMPOSITES

Hybrid composites are more advanced composites as compared to conventional FRP composites. Hybrids can have more than one reinforcing phase and a single matrix phase or single reinforcing phase with multiple matrix phases or multiple reinforcing and multiple matrix phases. They have better flexibility as compared to other fiber reinforced composites. By combining two or more types of fibers, it is possible to club the advantages of both the fibers while simultaneously mitigating their less desirable qualities. Normally, one of the fibers in a hybrid composite is a high-modulus and high-cost fiber such as carbon, boron and the other is usually a low-modulus fiber such as E-glass, Kevlar. The high-modulus fiber provides the stiffness and load bearing qualities, whereas the low-modulus fiber makes the composite more damage tolerant and keeps the material cost low. The mechanical properties of a hybrid composite can be varied by changing volume ratio and stacking sequence of different plies.

3.7.1 ADVANTAGES OF HYBRID COMPOSITES

- They offer better flexibility in the selection of fiber and matrix materials, which helps in better tailoring of the mechanical properties. For example the modulus, strength, fatigue performance etc of glass reinforced composites can be enhanced by inclusion of carbon fibers
- Better wear resistance
- Low thermal expansion coefficient
- Combination of high tensile strength and high failure strain
- Better impact and flexural properties
- Reduced overall cost of the composite
- Low notch sensitivity
- Non catastropic

3.7.2 TYPES OF HYBRID COMPOSITE

- DISPERSED FIBER- this consists of an inmate mixture of two or more types of continuous fiber aligned, but randomly dispersed throughout a common resin matrix. For example a very thin plate made up of alternating layers of various thickness of carbon and glass fiber tows laid across the width of the plate.
- DISPERSED FIBER PLY- This random or alternating mixtures of two or more types of fiber ply. The fiber plies may be unidirectional, angled, or built up from dispersed fiber material. The thickness of the material is not necessarily the same nor do equal thicknesses of the different fiber types have to be used. It can be both interply and intraply.
- FIBER SKIN AND CORE- This type consists of outer skins of one or more sorts of fiber laminate applied to a core made of another fiber laminate. Both skins and core may be

made of unidirectional or angle ply materials. It is usual, though not necessary to have the stiffer fiber in the skins and to have a structure which is symmetrical about a centre plane.

- FIBER SKIN, NON FIBER CORE- This type of hybrid, which consists of fiber skins applied to a core of foam, filled resin, some type of honeycomb, solid metal, wood, is often referred to as a sandwich structure. Materials of this type, though without high performance FRP skins, have been employed extensively for some years. The skins again may consist of one or more type of fiber arranged in a unidirectional or angle ply form of hybrids. The structures are usually symmetrical about a central plane, but need not necessarily be so. But can be with some core materials such as filled resin, solid metal, and wood strips of reinforcement.

3.8 APPLICATION OF HYBRIDS

- Helicopter rotor blades and drive shafts
- Ailerons and floor panels of aircrafts
- In automobile sector they are used in transmission units, chassis members, suspensions, and structural body parts of cars and lorries
- CFRP/ARP hybrids are used for making bicycle frames
- In sports industries Tennis racquets, fishing rods, skis, golf club shafts, yacht hulls, hockey sticks and paddles
- In medical world they are used for making orthoses

3.9 HYGROTHERMAL DIFFUSION [19]

Hygrothermal Diffusion usually takes place in presence of thermal and moisture gradients. In many cases water absorption obeys Fick's Law and diffusion is driven by the moisture concentration gradient between the environment and material producing continuous absorption until saturation is reached. The atoms migrate from region of higher concentration to that of lower concentration. The rate of diffusion increases rapidly with the rise in temperature. The concentration gradient of moisture is developed due to the non-uniform distribution of moisture. The presence of imperfections and internal stresses also accelerates the process of diffusion.

Epoxy resin absorbs water from the atmosphere from the surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of water into all the material. The water absorbed is not usually in liquid form but consists of molecules or group of molecules linked by hydrogen bonds to the polymer. In addition water can be absorbed by capillary action along any crack which may be present or along the fiber-matrix interface.

The Fickian diffusion process is influenced mainly by two factors:

(a) The internal (fiber volume fraction and its orientation)

(b) The external (relative humidity and temperature).

3.9.1 THEORY OF MOISTURE ABSORPTION

$$M = \frac{\text{WEIGHT OF SPECIMEN } - \text{ WEIGHT OF DRY SECIMEN}}{\text{WEIGHT OF DRY SPECIMEN}} \times 100$$
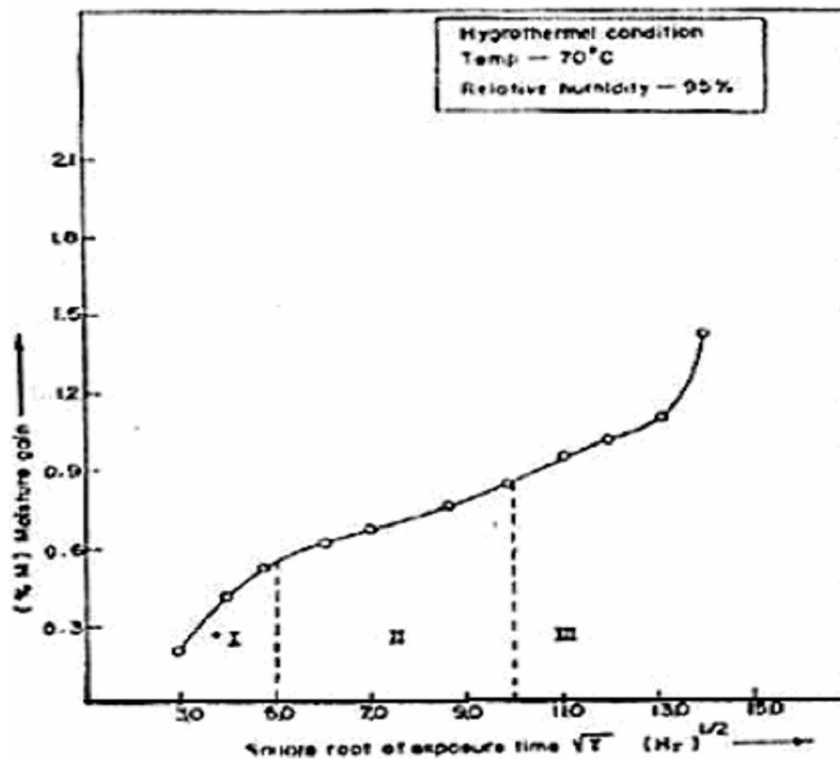

Fig 3.11 different stages of moisture absorption

Description of the different stages in moisture absorption kinetics:

- **Stage 1** moisture absorption is Fickian

- **Stage 2** there is deviation from linearity (reaching saturation so there is decrease in slope)
- **Stage 3** Total non-Fickian pattern (there is a development of micro cracks which enable rapid moisture diffusion, so rapid increase in percentage of moisture).

NON-FICKIAN BEHAVIOR

Fickian behavior is observed in the rubbery state of polymers but often fails to diffusion behavior in glassy polymers. The deviation from Fickian behavior occurs when:-

(a) Cracks or delamination develops.

(b) Moisture diffusion takes place along the fiber matrix interface.

(c) Presence of voids in the matrix.

The nature of diffusion behavior whether Fickian or non Fickian depends on the relative rate at which the polymer structure and the moisture distributions change. When the diffusion rates are much slower than the rate of relaxation, the diffusion has to be Fickian. Non Fickian behavior pertains to the situations when the relaxation processes progress at a rate comparable to the diffusion process. Hygrothermal diffusion in polymeric composites is mostly Fickian type, but non-Fickian behavior is also common for glass/epoxy composite. Absorbed moisture in the composite certainly deteriorates the matrix dominated properties but he effect is more pronounced at higher temperatures and at lower strain rates. The ILSS values are the most affected property due to this moisture absorption.

3.10 EFFECT OF HYGROTHERMAL TREATMENT ON GLASS TRANSITION TEMPERATURE T_g

Glass transition temperature (Tg) of thermo set matrix in composites is very importantproperty because it defines the critical service temperature of the component and consequently their applications. For practical applications they are used at a temperature below their Tg i.e. in the glass state. When materials are exposed to hydrothermal environment, the Tg usually decreases and therefore, the service temperature of the material changes. Moisture absorption by epoxy

matrix composites has plasticizer effect, as reduction of Tg of the matrix. This effect is usually reversible when water is removed but exposure to high temperature can produce irreversible effects, which is attributed to the chemical degradation of the matrix and attack on the fiber/matrix interface. This causes increase of internal voids of the entangling polymer chain, promoting chain expansion and the micro-cracks formation into the polymer matrix [17, 18]. There are many factors on which moisture absorption depends such as temperature, fiber volume fraction, reinforcement orientation, fiber nature (i.e. permeability, polarity, and density), and area of exposed surfaces, diffusivity and surface protection.

3.11 3-POINT BEND TEST

The FRP is subjected to three – point bending until the layers delaminates. When this occurs, the stiffness of the specimen as a whole decreases, which translates as a drop in load in the load - displacement curve? The three-point bend fixture should include two 5 mm diameter supports forming a 36 mm span and a 10 mm diameter load application roller set in the middle of the span. The crosshead speed is 0.5 mm/min unless otherwise specified. Test should be performed at 23 ± 2 °C. The three point bending flexural test provides values for the modulus of elasticity in bending E_B The flexural stress σ_f, flexural strain ε_f, and the flexural stress- strain response of the material. The main advantage of a three point flexural test is the ease of specimen preparation and testing. However, this method has also got some disadvantages such as the results of testing method are sensitive to specimen and loading geometry and strain rate.
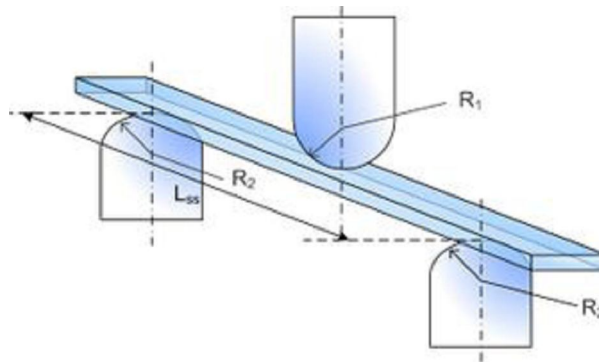

Fig 3.12 flexural test setup

Calculation of the flexural stress, flexural strain and young's modulus :

FLEXURAL STRESS:

$$\sigma_f = \frac{3PL}{2bd^2}$$

FLEXURAL STRAIN

$$\epsilon_f = \frac{6Dd}{L^2}$$

YOUNG'S MODULUS

$$E_B = \frac{L^3 m}{4bd^3}$$

- σ_f = Stress in outer fibers at midpoint, [MPa]

- ϵ_f = Strain in the outer surface [%]

- E_f = Modulus of elasticity in bending [MPa]

- P = load at a given point on the load deflection curve [N]

- L = Support span [mm]

- b = Width of test beam [mm]

- d = Depth of tested beam [mm]

- D = maximum deflection of the center of the beam [mm]

- m = Slope of the tangent to the initial straight-line portion of the load deflection curve [N/mm]

3.12 MODES OF FAILURE

Damage in a polymer composite can be caused during manufacturing or during service. Improper laminate fabrication or curing procedures can induce defects in the form of delamination, voids, debonds, wrinkles, inclusions, broken fiber, and fiber misalignment. The manufacturing defects may also be introduced by machining the components for fastener holes, design cutouts, and so on [20, 21]. The service damage in a composite structure (e.g., an aircraft) may result from the impact by runway debris, hailstones, bird strike, and ground service vehicles etc. impact damage

can also be caused by dropping tools accidentally during maintenance. The principal modes of failure are:

- Delamination

- Fiber breakage

- Matrix cracking

- Debonding

3.12.1 <u>DELAMINATION</u>

Delamination is the separation of plies of a laminate. The delamination in composites is caused by interlaminar stresses produced by out of plane loading (e.g., impact) eccentricities in load paths or discontinuities in the structure. Matrix cracking in off-axis plies may generate interlaminar stresses to promote delamination. REIFSNIDER estimate that in quasi isotropic laminates, these interlaminar stresses occur near the crack tip of the matrix. These interlaminar stresses tend to cause local delamination that grows along ply interfaces near matrix cracks. The magnitude depends upon the materials used, stacking sequence, laminate shape, or type of loading.

<u>EFFECTS OF DELAMINATION</u>

- Reduction in stiffness

- Reduced strength

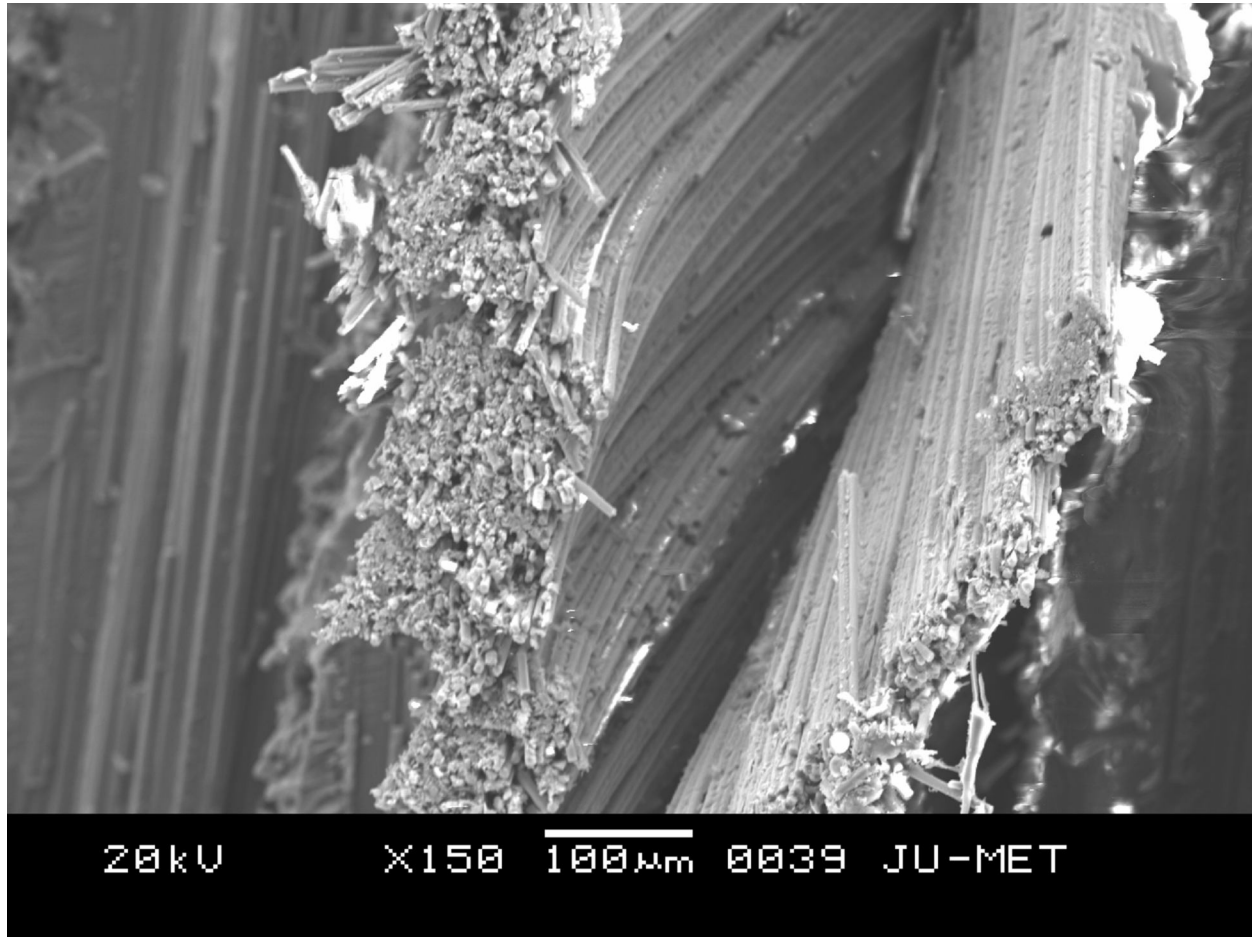- Reduced rate of resistance to fatigue

Fig 3.13 showing extensive delamination [21]

3.12.2 <u>FIBER BREAKAGE</u>

Fiber breakage occurs either by overloading or extensive strain. Because polymer matrix composites generally have greater strain to failure values than the fibers used, this damage mechanism is seen quite frequently. Stress concentration from matrix cracks and fiber-matrix debonding can also provoke fiber breakage. Fiber breakage is usually seen in composites containing brittle carbon fibers. Fiber breakage is an extensive mode of failure during high strain rate loading [22, 23].
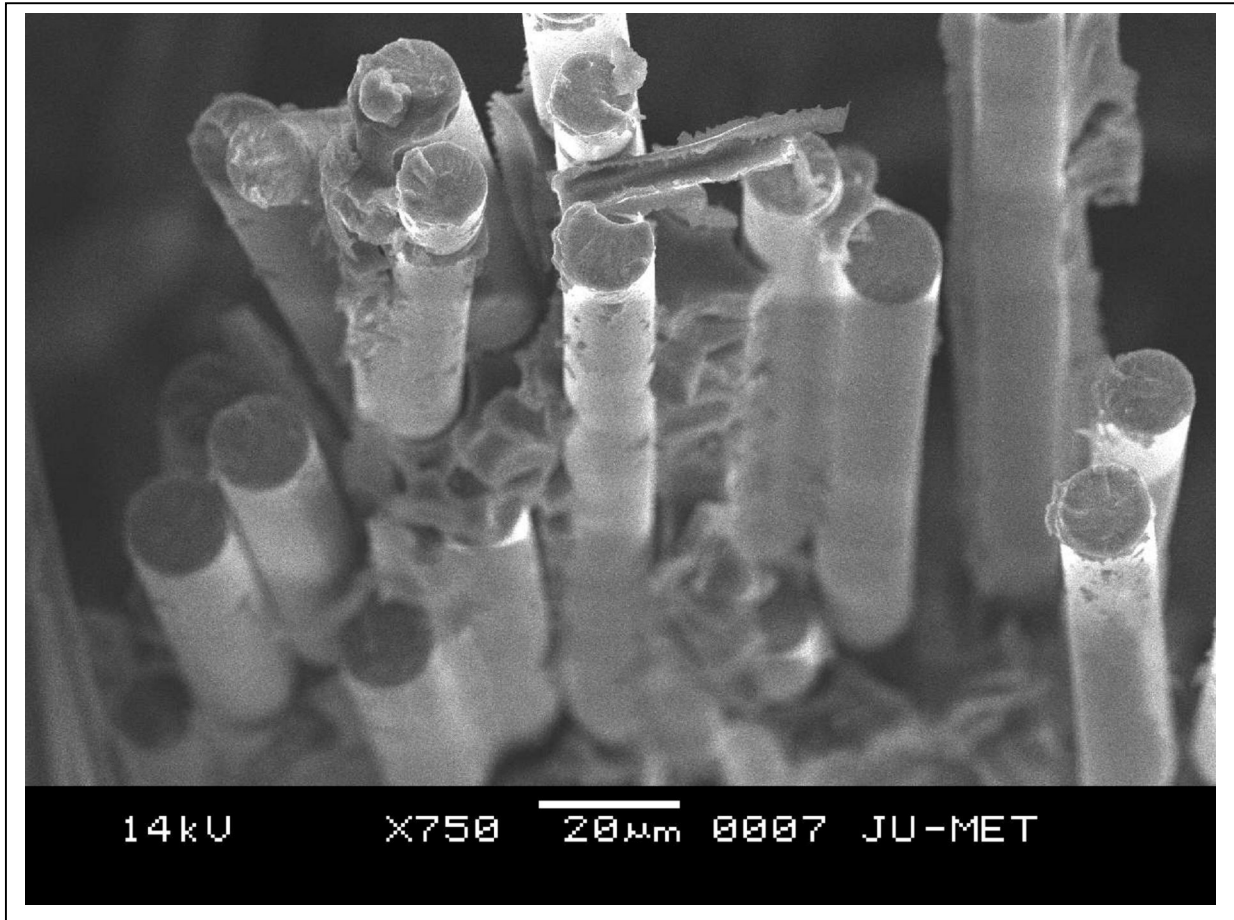
Fig 3.14 showing extensive fiber breakage at high strain rates [21]

3.12.3 <u>MATRIX CRAKING</u>

Matrix cracking is characterized by microscopic cracks that form predominantly in the matrix areas of laminate under loading. Their orientation may be in any direction depending on the applied stress. In multidirectional laminate, matrix cracks will appear first in the weakest ply then subsequently with increase in stress propagates to the strong layers. Matrix cracks are initiated early in the process of fatigue. The stacking sequence and the stress distribution near the fiber matrix interface play an important role in failure by matrix cracking. Moisture absorbed

also contributes towards matrix cracking, due to difference in coefficients of volume expansion of fiber and matrix stresses are generated, which is accountable for matrix cracking.
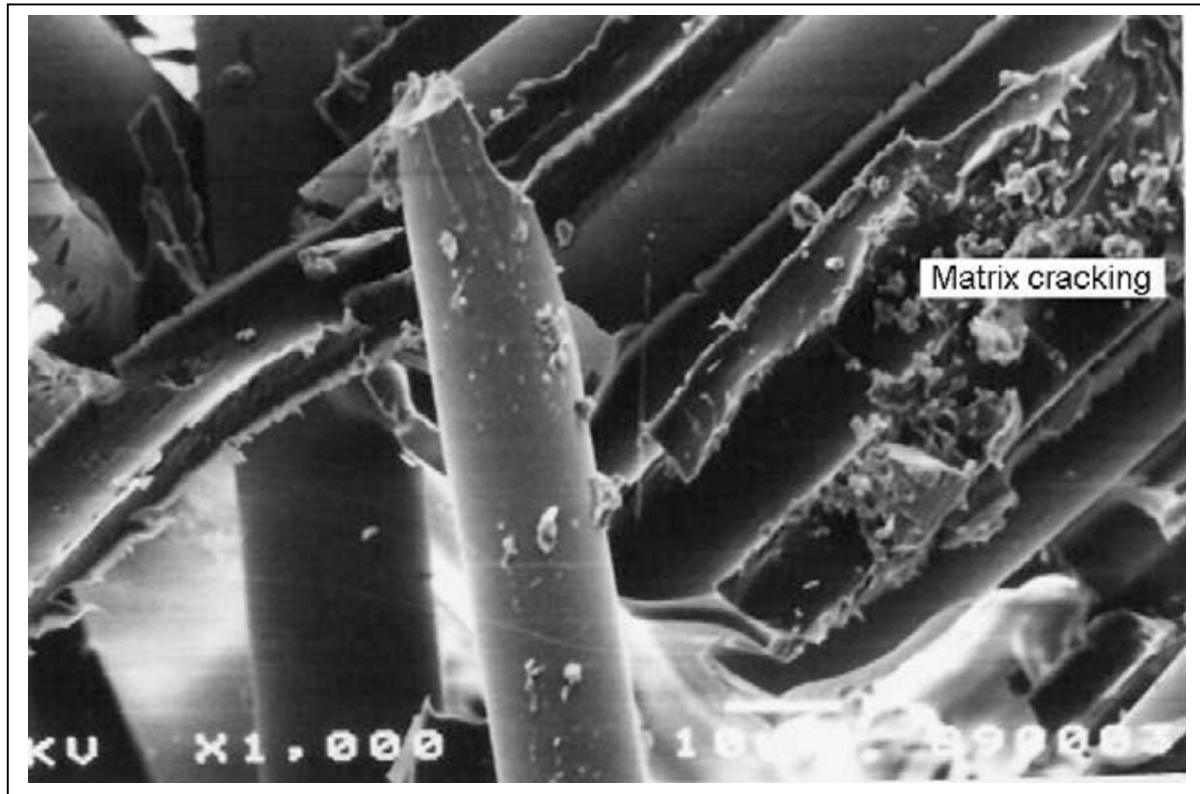

Fig 3.15 showing matrix cracking [22]

3.12.4 DEBONDING

Debonding occurs due to the interfacial shear stress components. The extent of debonding is decided by the boding between the matrix and the fibers. High interfacial bond strengths will permit little or no fiber matrix interfacial debonding. In contrast with low bond strength may exhibit large areas of interfacial debonding that combines with or intensifies other damage mechanisms to speed up failure. The average bond strengths between an epoxy resin and few

commonly used fibers are 33 MPa for E-Glass, 49MPa for E-Glass+ silanes, 38 MPa for Kevlar and 57 MPa for celion carbon fibers.
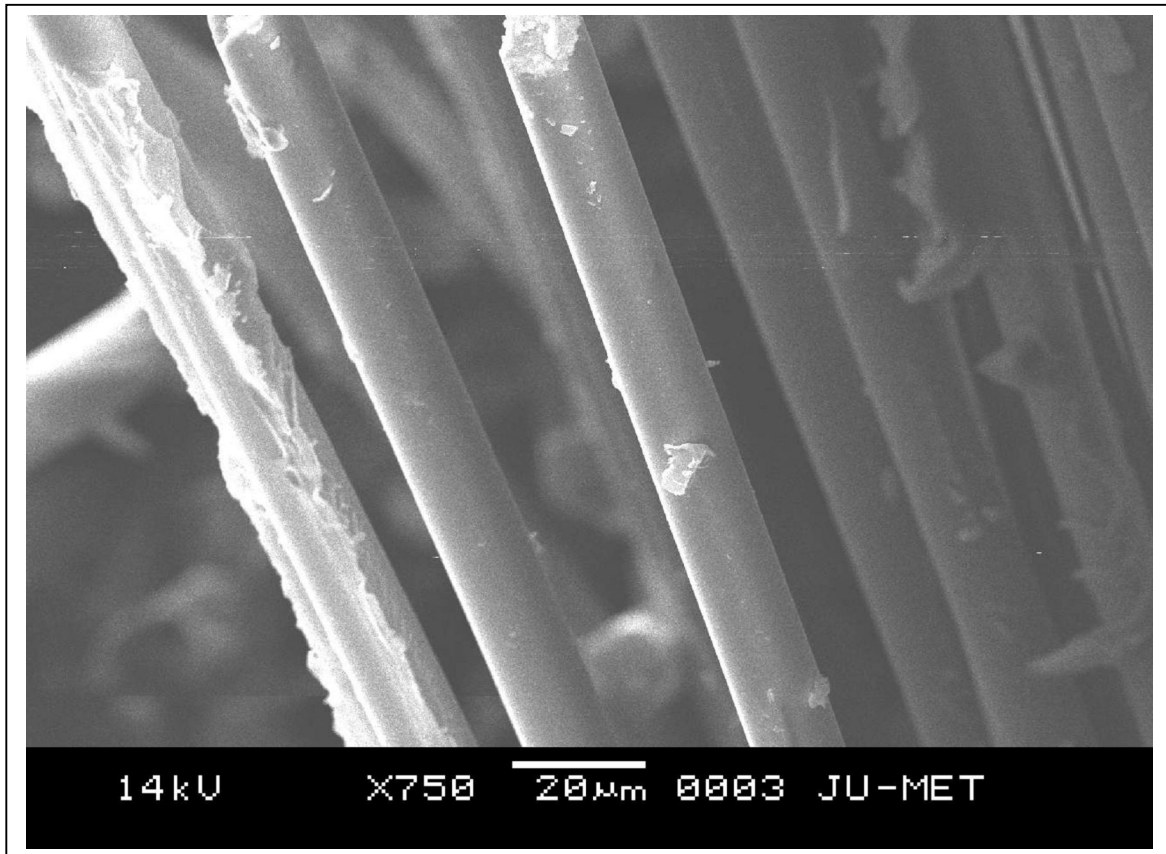

Fig 3.16 showing debonding [22]

4. EXPERIMENTATION

4.1 *MATERIALS*

Woven fabric Carbon fibres (T-300 PAN based, High Strength), E-glass (FGP, RP-10) of density 0.36kg/m^2 and epoxy adhesive (Bisphenol A type, Ciba-Geigy LY 556 araldite, hardener HY-951) were used to fabricate composite laminates.

4.2 *FABRICATION OF COMPOSITE*

The glass fibre and carbon fibre were cut to standard size square sheets. According to ASTM standards for proper determination of interlaminar shear strength (ILSS), a minimum of sixteen fibre plies should be used. The plies were then weighed and equal amount of Araldite LY-556, an unmodified epoxy resin based on Bisphenol A and hardener (Ciba-Geigy, India) HY951 (10% of epoxy taken) a primary aliphatic amine were mixed in a bowl using a glass rod. Care was taken to avoid entrapment of air bubbles. Because the air bubbles trapped in the matrix will result in void formations, which result in concentration of stress and thereby resulting in crack formation.
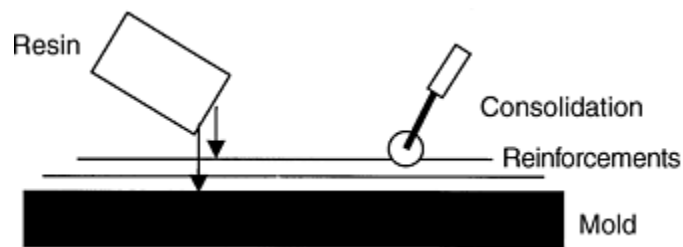

Fig 4.1 Hand layup process

The milder sheet or release sheet was than laid on a flat surface, on to which mold release spray was sprayed, then a layer of epoxy was coated on the sheet, now alternately, layers of carbon

fibre fabric and glass fibre fabric were laid upon other, with a layer of resin in between such fabric. The stacking sequence was maintained. At the last again a milder sheet was taken and mold release sprayed on to it, and then a layer of resin mix was applied to it and this was put on to the last layer of composite. A flat board was then put on these sheets and dead loads were applied on to this prepared composite above this board, and the whole was then allowed to cure for around 72 hours, after which the prepared sample was ripped off the mold.

4.3 *SPECIMEN PREPARATION*

The laminates were cut into short beam shear test specimen using a diamond tipped circular cutting saw, where the specimens have width 13mm and length 70 mm, for conducting 3 point bend test which is in accordance with the ASTM D 2344-84 (1989) standard. Where the length of the specimen should be greater than 10 times the thickness and maximum width given as D+2t, where D is 10 and t is the thickness of the composite. And the span length was maintained 40mm while testing.

4.4 *MOISTURE REMOVAL*

Before exposing the specimens to any sort of environment, moisture should be removed completely. This was done by putting the specimens into a baking oven held at a temperature of 60^0C after taking the initial weights. After baking the specimens for an hour they were taken out and weights were taken. These steps were continued until there is no change in the weight or till the specimens have constant weight.

4.5 *ENVIRONMENTAL CONDITIONING*

4.5.1 *HYGROTHERMAL CHAMBER*

A humidity chamber was used for hygrothermal treatment. Once the chamber is switched on sufficient time gap was allowed till the required humidity and temperature was attained (R.H=95%, TEMP=60^0C).

Fig 4.2 Hygrothermal chamber

Precautions were taken to maintain the level of distilled water in the tank at the desired level, also the distilled water level for the wet bulb thermometer was kept at appropriate level. The net temperature fluctuation was 0.7^0C, while the humidity fluctuation ranged up to a maximum of 0.4 percent. Then the samples were put into the chamber and subsequently removed after predetermined time periods (24hrs, 48hrs, 72hrs, 96hrs, and 120hrs). After the hygrothermal treatment was over each specimen is weighed by an electronic balance (corrected up to 4 places of decimal) after wiping the specimens clean using a tissue paper so that no excess moisture

remains on the surface. Specimens were then wrapped in aluminium foil so as to avoid moisture loss or moisture pickup. The % moisture uptake was given by the expression given below:

$$M = \frac{WEIGHT\,OF\,SPECIMEN \; - \; WEIGHT\,OF\,DRY\,SECIMEN}{WEIGHT\,OF\,DRY\,SPECIMEN} \times 100$$

4.5.2 *CRYOGENIC CONDITIONING*

The cryogenic conditioning was done at a temperature of -40^0C in a double compressor fitted deep freezer. The specimens were put into the chamber and held for 2 hours. Care was taken while putting the samples in and taking out the specimens.

4.5.3 *THERMAL CONDITIONING*

The thermal conditioning was done in a baking oven held at 50^0C. Sufficient time was given after the temperature of the oven reached the set temperature so that there is uniform temperature throughout the oven. The specimens were held for 2 hours after which they were wrapped in aluminium foil and were taken for 3 point bend test.

4.6 *THREE POINT BEND TEST*

After the Hygrothermal treatment, cryogenic conditioning and thermal conditioning the dimensions of all the samples were measured and then they were tested for determination of ILSS by 3-Point bend test. This test was performed on INSTRON-1195 in accordance with ASTM D 2344-84 standard. The samples were loaded and the loading rate used was 1 mm/min and the loads vs. displacement graphs were obtained. From these graphs, the ILSS value for each specimen was calculated using the formula:

ILSS = (0.75 x P) / (W x T)

Where: P = Breaking load (KN)

W = Width of the specimen (mm)

T = Thickness of the specimen (mm)

Fig 4.3 INSTRON 1195

Fig 4.4 Short Beam Shear test set up, loading of the sample

4.7 *DIFFERENTIAL SCANNING CALORIMETRY*

The DSC measurements were performed on a Mettler-Toledo 821 with intra cooler, using the STAR software with Alternating DSC (ADSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In. The underlying heating rate of 10^0C/min was used. In order

to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. Standard aluminum pans were used. The experiments were performed in the temperature range from 40^0C to 120^0C.
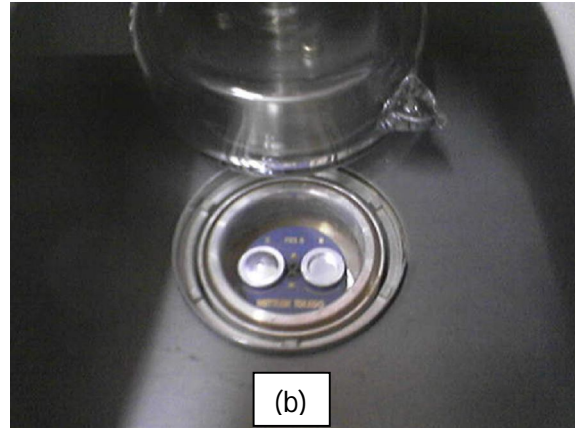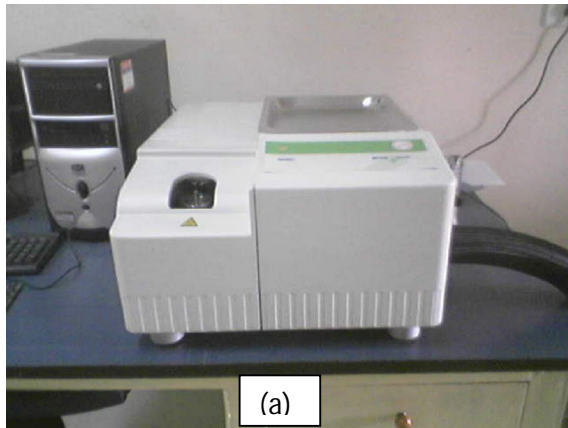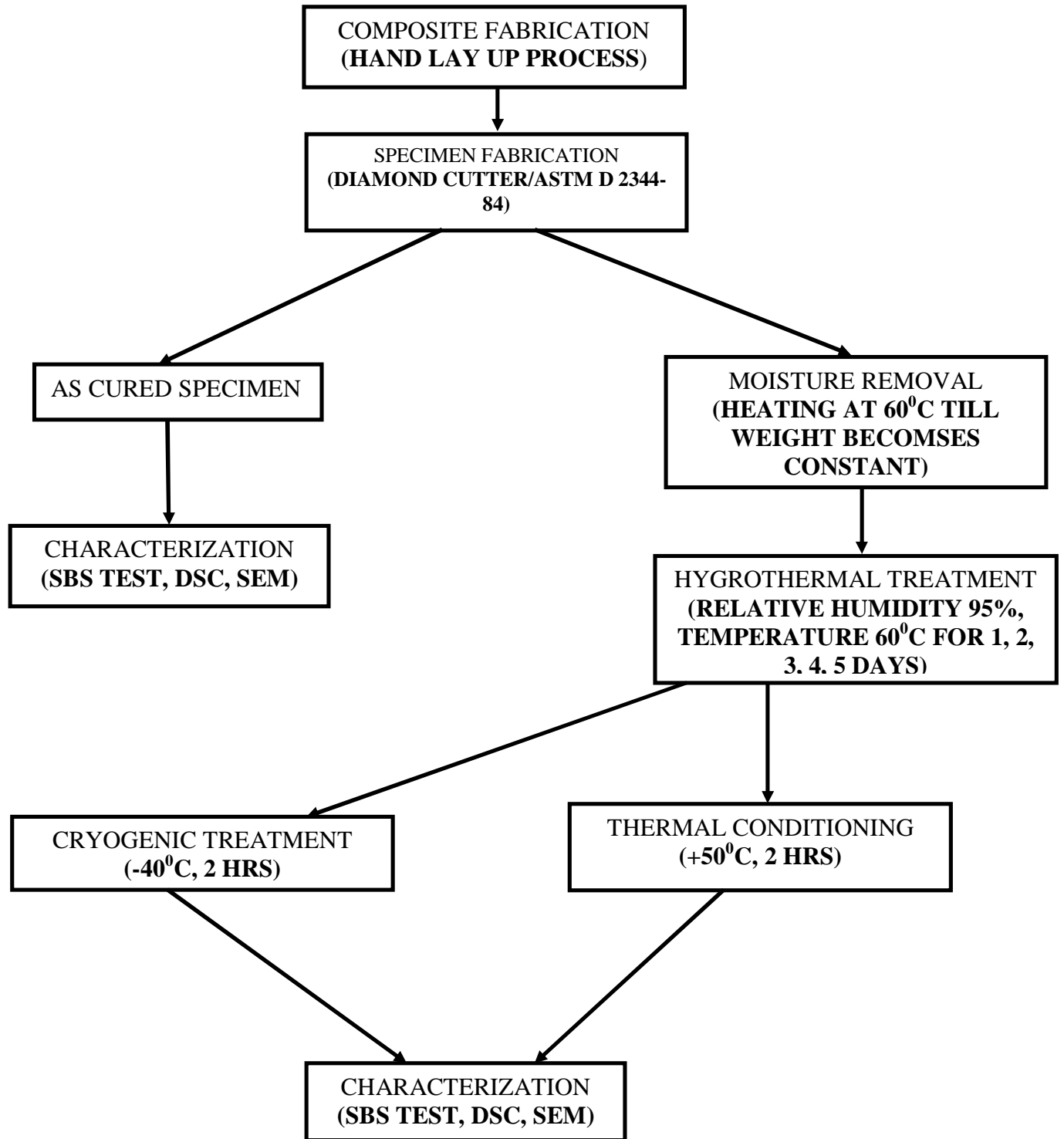

Fig 4.5(a) Mettler-Toledo 821 with intra cooler for DSC measurements and (b) reference-sample chamber

From the DSC results variation of Tg with moisture absorption was found out.

4.8 *SCANNING ELECTRON MICROSCOPY*

To study the fracture surface of the samples treated as discussed above, microscopy was carried out using a JEOL-JSM 6480 LV scanning electron microscope and thus the micrographs obtained were used to ascertain the effect of moisture on the mode of failure and hence the mechanical properties. The samples were loaded onto the sample holder and placed inside the SEM, adjusting the working distance and hence the spot size the chamber was closed and vacuum was applied. Micrographs were taken from revealing sites.

4.9 *BRIEF OVERVIEW OF EXPERIMENTATION*

COMPOSITE FABRICATION
(HAND LAY UP PROCESS)

SPECIMEN FABRICATION
(DIAMOND CUTTER/ASTM D 2344-84)

AS CURED SPECIMEN

MOISTURE REMOVAL
(HEATING AT 60^{0}C TILL WEIGHT BECOMSES CONSTANT)

CHARACTERIZATION
(SBS TEST, DSC, SEM)

HYGROTHERMAL TREATMENT
(RELATIVE HUMIDITY 95%, TEMPERATURE 60^{0}C FOR 1, 2, 3. 4. 5 DAYS)

CRYOGENIC TREATMENT
(-40^{0}C, 2 HRS)

THERMAL CONDITIONING
(+50^{0}C, 2 HRS)

CHARACTERIZATION
(SBS TEST, DSC, SEM)

5. RESULT AND DISCUSSIONS

5.1 _MOISTURE ABSORPTION_

SAMPLE NO	TIME OF EXPOSURE (HOURS)	% MOISTURE UPTAKE	AVERAGE UPTAKE
1	24	0.80321	
2	24	0.88832	0.84576
3	48	0.95465	
4	48	0.94537	0.95001
5	72	1.48462	
6	72	1.41752	1.45107
7	96	1.50637	
8	96	0.98146	1.243915
9	120	1.80412	
10	120	1.27167	1.27167

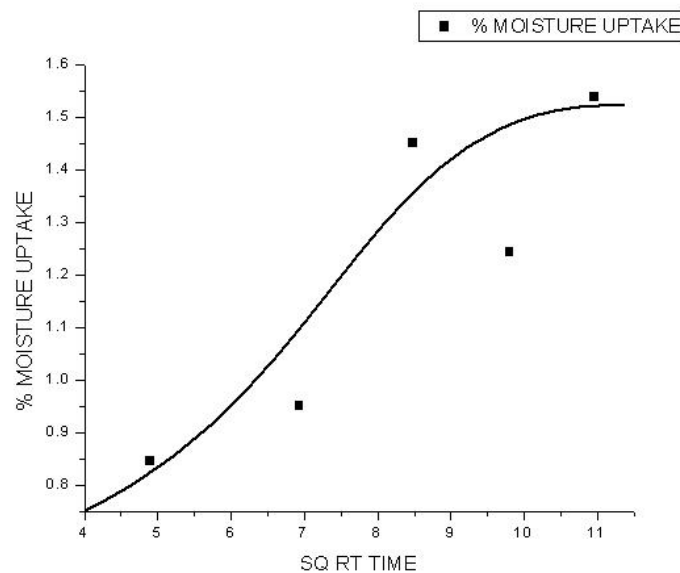Table 5.1 variation of moisture uptake with time

Fig. 5.1 variation of % moisture with square root time

From the graph it can be seen that the rate of absorption of moisture is quite high which is due to the presence of empty spaces or voids, the moisture absorption curve is in accordance with the fick's 2nd law hence the moisture absorption is fickian. After a specific time the rate of moisture absorption decreases gradually. This is due to the saturation of the matrix i.e. the moisture absorbed is sufficient enough to fill the spaces and very less moisture is required. Thus it can be concluded that the initial rate of moisture absorption is very high and it gradually becomes saturated at higher time periods, but if further exposure is done there will be more uptake of moisture due to generation of cracks due to swelling of the matrix and the moisture absorption will not follow the fick's laws and therefore the moisture absorption can be mentioned as non fickian.

5.2 *VARIATION OF ILSS WITH CONDITIONING*

5.2.1 *CRYOGENIC CONDITIONING AFTER HYGROTHERMAL TREATMENT*

Samples treated for 2 hours at -40⁰C

SAMPLE NO	TIME OF HYGROTHERMAL TREATMENT(HRS)	% MOISTURE	ILSS (MPa)
1	24	0.88832	28.209
2	48	0.94537	29.789
3	72	1.41752	26.577
4	96	0.98146	29.771
5	120	1.27167	30.888

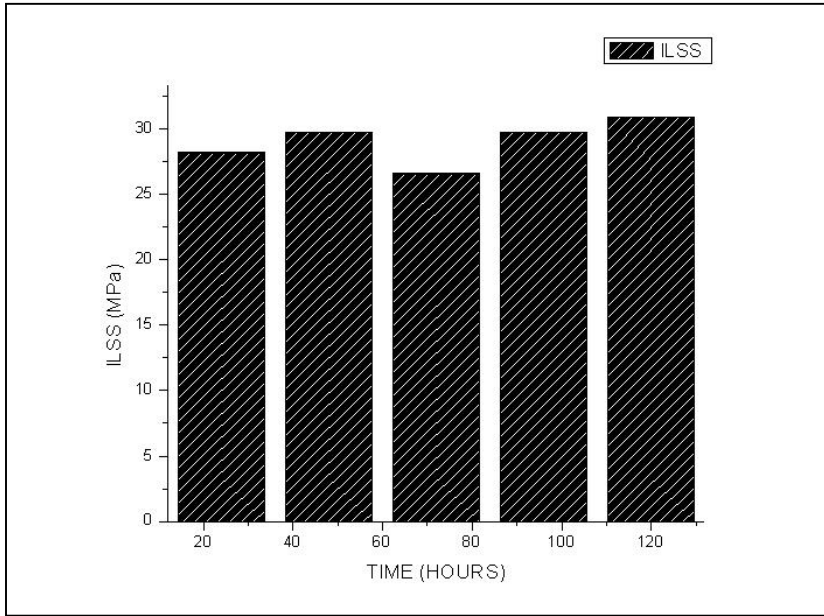Table 5.2 variation of ILSS with % of moisture for samples treated at -40^{0}C for 2 hrs

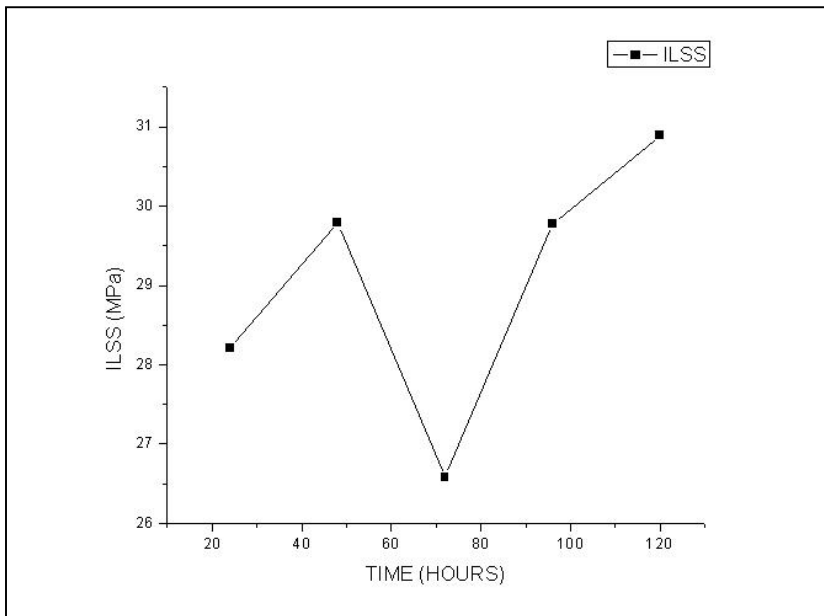Fig 5.2 Extent of variation of ILSS with time of exposure for samples treated at -40^{0}C for 2 hrs

Fig 5.3 Nature of variation of ILSS with time of exposure for samples treated at -40^{0}C for 2 hrs

From the graphs it can be seen that seen that initially there is an increase of the shear strength with falls at a point and then gradually rises. At low temperature the movement of the polymer chains is restricted and also there is mechanical keying which accounts for the rise in the ILSS values but the fall may be due to excess absorption of moisture due to which the swelling of the

matrix might have occurred eventually resulting in poor interfacial bonding between the fibre and the matrix. The rise in ILSS values at higher exposure time is not much because the amount of moisture absorbed towards higher time is nearly same. Whereas the samples which were untreated showed a higher values of ILSS which might be due to absence of moisture; which weakens the interface between the fibre and matrix.

5.2.2 *THERMAL CONDITIONING AFTER HYGROTHERMAL TREATMENT*

Samples treated for 2 hours at 50^0C

SAMPLE NO	TIME OF HYGROTHERMAL TREATMENT(HRS)	% MOISTURE	ILSS (MPa)
1	24	0.80321	26.7212
2	48	0.95465	29.2549
3	72	1.48462	25.9673
4	96	1.50637	30.2717
5	120	1.80412	29.7371

Table 5.3 variation of ILSS with % of moisture for samples treated at 50^0C for 2 hrs
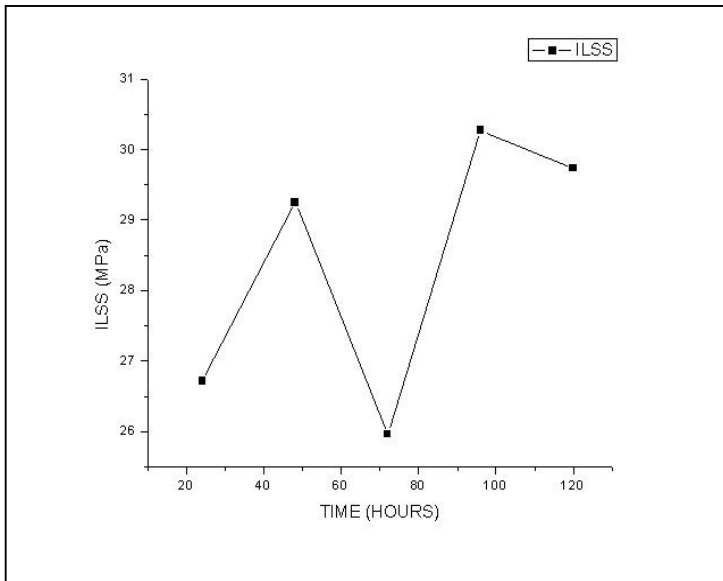
Fig 5.4 Nature of variation of ILSS with time of exposure for samples treated at 50^0C for 2 hrs
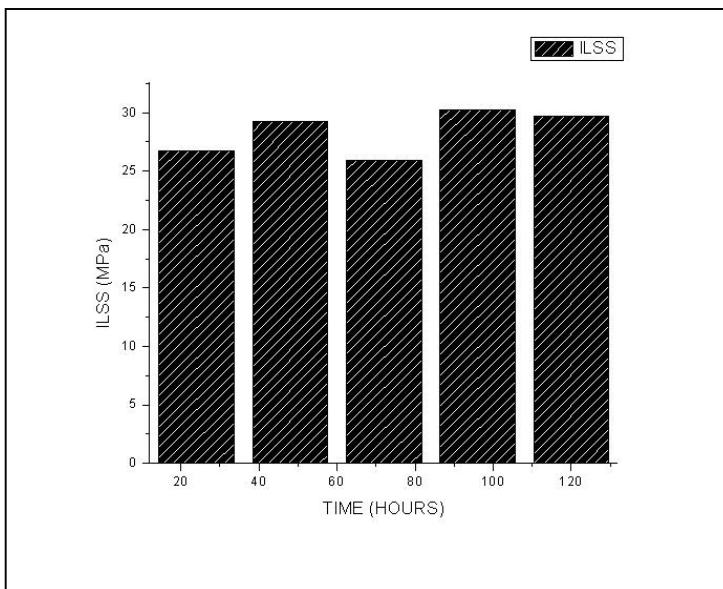

Fig 5.5 Extent of variation of ILSS with time of exposure for samples treated at 50^0C for 2 hrs

For the above curves and bar diagrams it can be seen that the shear strengths values show an initial increase which might be due to removal of moisture and mitigation of stresses generated due to volumetric expansion and at higher time of exposure the ILSS values show a decrement which might be due to formation of voids due to removal of moisture, thereby creating a discontinuity in the matrix which causes improper stress transfer to the fibres[21]. But in the

nature of variation plot it can be seen that there is a sudden dip in ILSS values at 72 hours which might be due to presence of high amount of voids caused due to fabrication error.

5.3 *COMPARISION OF ILSS VALUES FOR THERMALLY AND CRYOGENICALLY TREATED HYGROTHERMALLY CONDITIONED HYBRIDS WITH THE AS CURED VALUES*
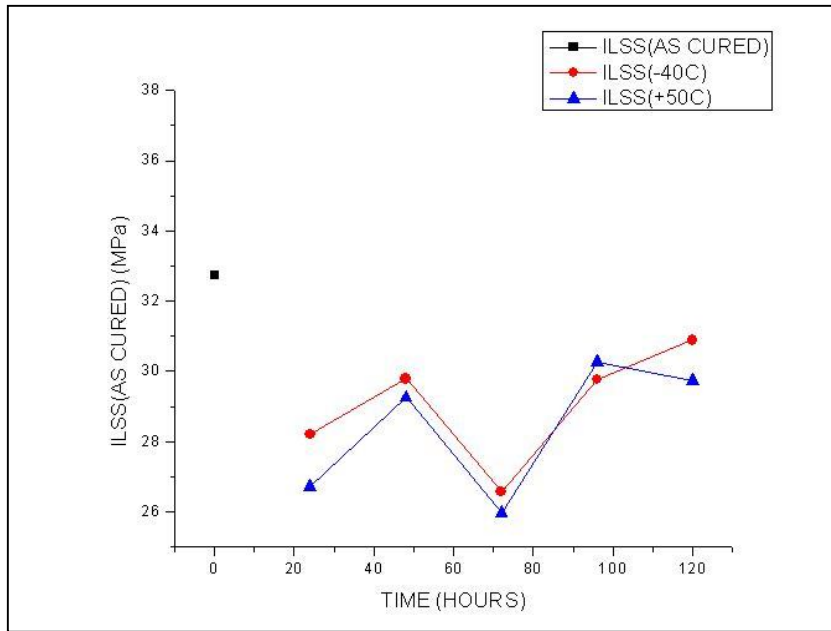

Fig 5.6 variation of ILSS for differently treated specimens and for as cured specimen

In general ILSS decreases with increase in hygrothermal exposure time, apart from the initial increase due to the further polymerization of the epoxy matrix. Prolonged exposure creates a high degree of hygroscopic stress which may result in micro crack coalescence and crack blunting leading to increase in ILSS. But with further increase in exposure time, there is in general a decrease in ILSS values, while the moisture absorption kinetics changes from fickian to non-fickian. Upon thermal treatment after hygrothermal treatment a similar phenomena as in hygrothermal for lower exposure times is observed. However longer exposure causes the mechanical property deterioration due to the formation of micro cracks and crazing (more misfit stresses are generated due to differential Coefficient of thermal expansion of the fibres and the matrix. Whereas the initial increase in strength of cryogenically treated specimen is attributed to

the matrix hardening but for longer exposures the strength decreases due to the interaction of stress concentration at the defect tip (upon volumetric expansion caused due to moisture to ice transformation). Whereas the As-cured specimens showed a high degree of integrity as the ILSS values are much higher than the treated samples.
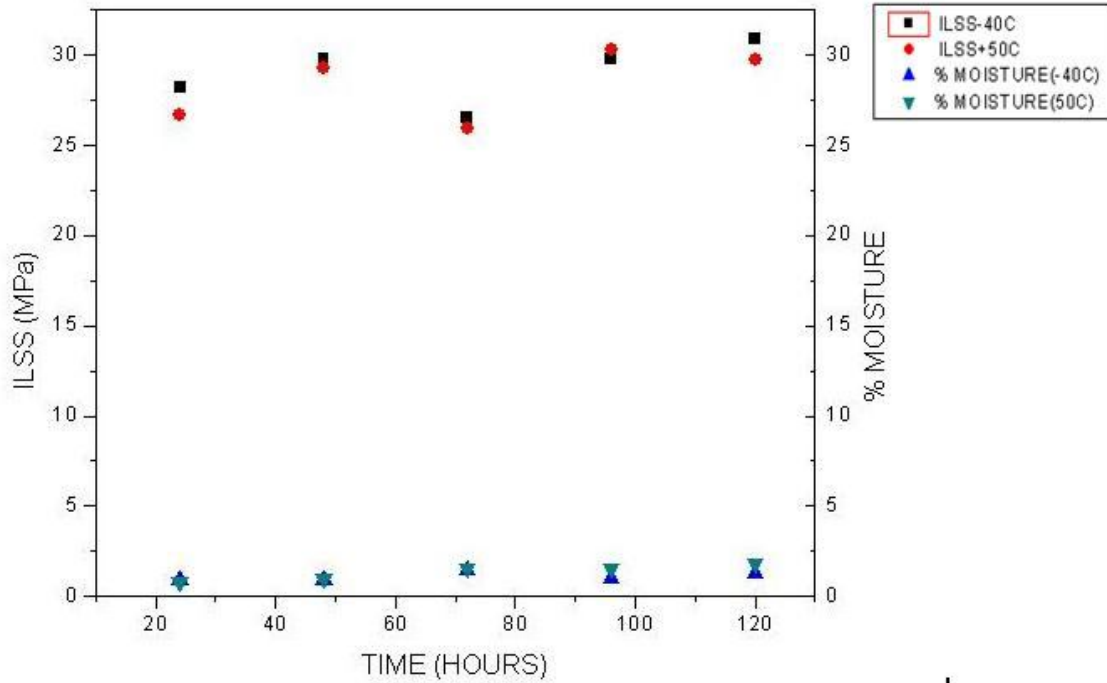

Fig 5.7 *VARIATION OF ILSS AND MOISTURE PICKUP FOR DIFFERENTLY TREATED SPECIMENS AT DIFFERENT EXPOSURE TIMES*

5.4 *EFFECT OF MOISTURE CONTENT ON Tg*

SAMPLE NO	TREATMENT	Tg
1	As-Cured	85.84
2	Hygrothermal 72 hrs + -40^{0}C 2 hours	96.18
3	Hygrothermal 72 hrs + 50^{0}C 2 hours	83.19

Table 5.4 Variation of Tg with treatment

^exo   **As Cured UKM**   **02.07.2009 16:04:57**

Method: 40 -130@10
40.0-130.0°C 10.00°C/min   N2 40.0 ml/min   As-Cured 2ndrun, 02.07.2009 15:36:01
As-Cured 2ndrun, 16.8000 mg

2 mW

Glass Transition
Onset   74.75 °C
Midpoint   85.84 °C

MME NIT Rourkela: METTLER   **STAR^e SW 8.10**
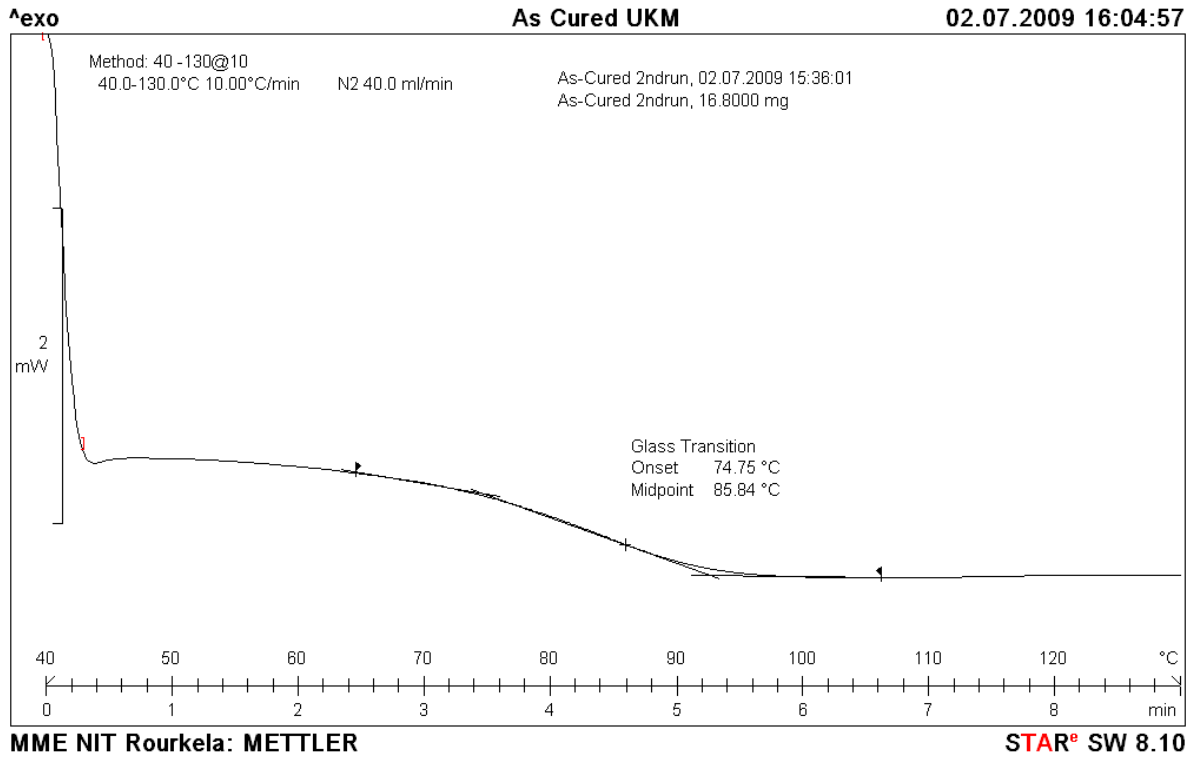
Fig 5.8 DSC curve for As-Cured specimen

^exo   **Hygro40 UKM**   **02.07.2009 16:09:31**

Sample10 Hygro40, 02.07.2009 16:05:42
Sample10 Hygro40, 26.2000 mg

5 mW

Glass Transition
Onset   92.34 °C
Midpoint   96.18 °C

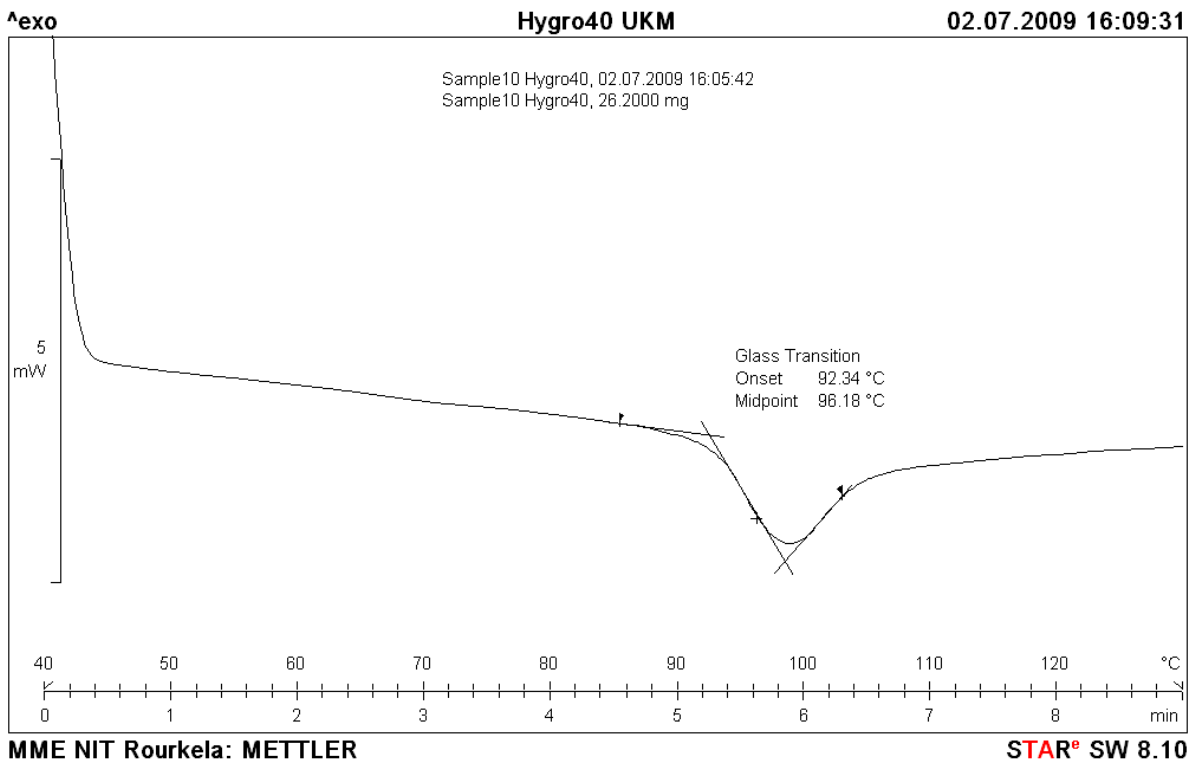**MME NIT Rourkela: METTLER**   **STAR^e SW 8.10**

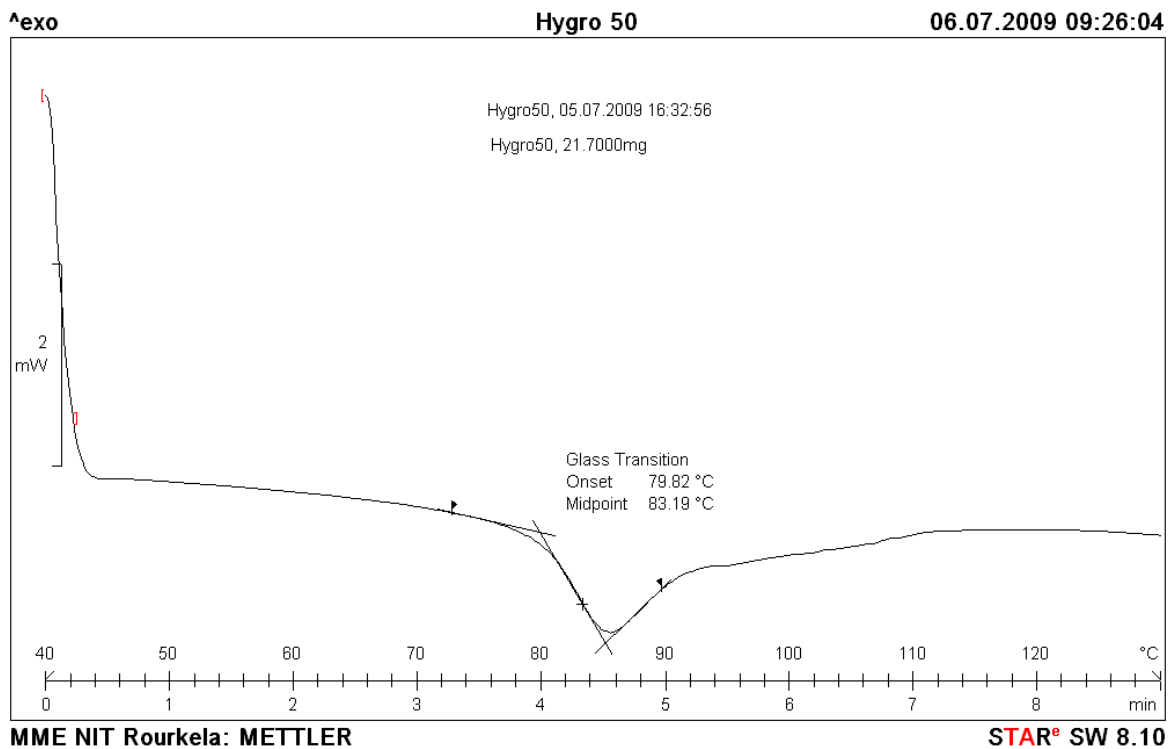Fig 5.9 DSC curve for specimen treated 72 hrs hygrothermally then subjected to -40^{0}C for 2Hrs

Fig 5.10 DSC curve for specimen treated 72 hrs hygrothermally then subjected to 50^0C for 2Hrs
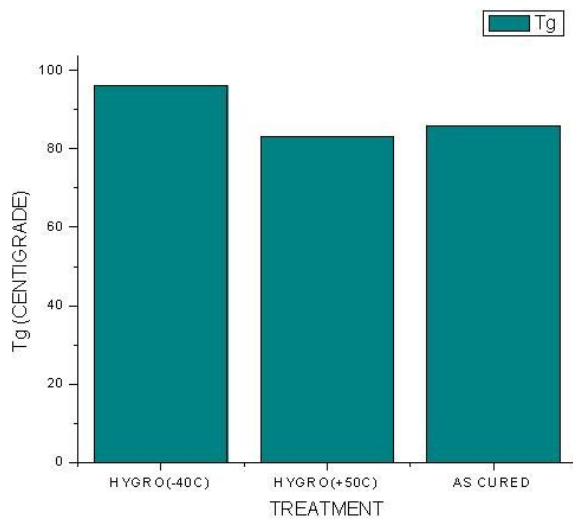

Fig 5.11 plot showing the variation of Tg with treatment

From the above plot we can see that the specimen subjected to hygrothermal treatment along with cryogenic conditioning, there is an increase in Tg. Here the number of hours of treatment given is low hours hygrothermal treatment and due to the cryogenic treatment the moisture gets entrapped. So in this case hydrolysis pre dominates plasticization. Due to hydrolysis there will be scission of polymer chains. There is breakage of covalent bonds and the absorbed water molecules form strong hydrogen bonds with the hydrophilic groups of the epoxy network[23]. Water with double hydrogen bonds acts as a physical crosslink. Due to the formation of hydrogen bonds, there is an increase in Tg. But in case of the specimen treated hygrothermally for 72 hrs and then subjected to thermal condition, the Tg is nearly equal to that of the As-Cured specimen. This might have happened due to removal of the moisture from the sample due to prolonged exposure at intermediately high temperature.
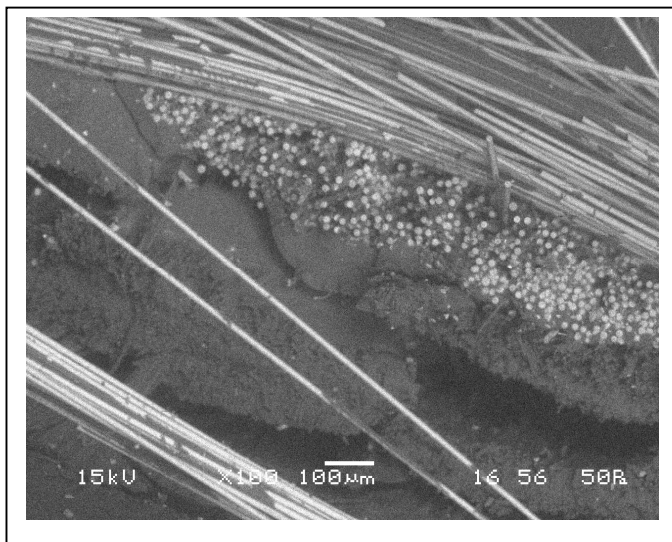
5.5 *SEM ANALYSIS*

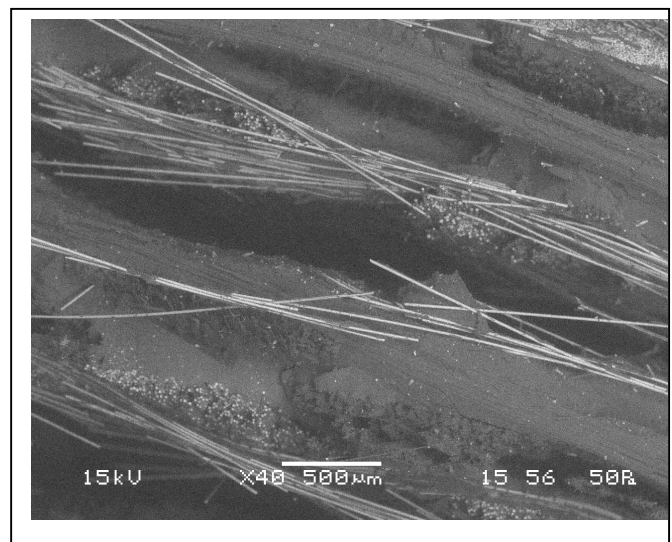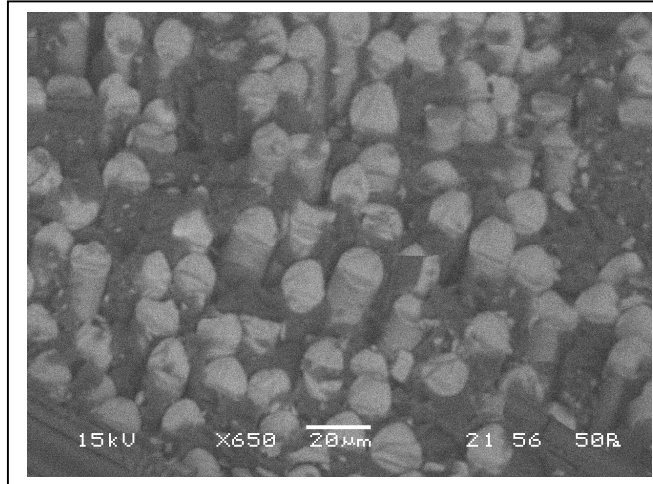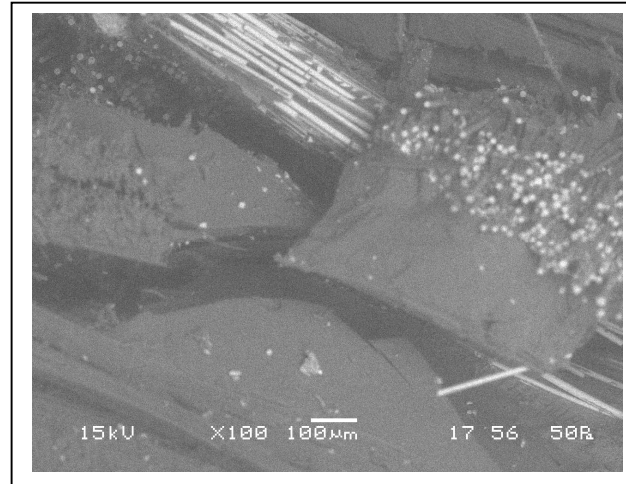Fig 5.12   fig 5.13

Fig 5.14

fig 5.15

The common feature of all the SEM micrographs shown above is fiber breakage. In fig 5.12 the modes of failure are mainly matrix cracking fibre breakage and fibre pullout. The fibre breakage occurs when the fibres are unable to sustain the load applied. But matrix cracking occurs mainly due to the matrix hardening when subjected to cryogenic environments. But fibre pull out is a case which occurs due to improper bonding between the fibre and the matrix due to which there is ineffective load transfer to the fibres from the matrix and hence due to stress accumulation at the interface the fibres are pulled out of the matrix. The fig 5.13 shows extensive delamination along with fibre fracture which might have occurred due to high moisture intake or higher exposure to hygrothermal exposures. Delamination may also occur due to the presence of voids at the interface (due to fabrication error), when stress is applied, a triaxial state of stress is developed ahead of the void and hence crack propagates along the interface of fibre and matrix causing failure of the composite. Fig 5.13 is a case where the specimen is subjected to cryogenic environment, it can be seen that there is a high degree of adhesion at the fibre matrix interface which is mainly due to the free thaw effects or mechanical keying [24]. Whereas fig 5.14 is a pure case of extensive matrix cracking caused due to excess moisture uptake.

6. CONCLUSION

Any composite material, when exposed to hygrothermal environment, always absorbs moisture, and this leads to deterioration of mechanical properties. The amount of moisture absorbed increases with increase in time of hygrothermal treatment. For low Hours treatment—Hydrolysis predominates, while for high hour treatment—plasticization predominates.

In this experiment the composites were subjected to moisture for lower duration of time so due to hydrolysis, there is hydrogen bond formation and hence increases Tg.

The mechanical properties were found to be higher in case of specimens subjected to cryogenic conditioning after hygrothermal treatment than the specimens which were subjected to thermal conditioning after hygrothermal treatment.

Higher the Tg, better is the response of the material to the working conditions, and the material retains dimensional stability even at higher temperatures. Hence higher the Tg, better will be the mechanical properties.

By focusing on the physical changes that take place at the interface, we can infer about the causes for change or deterioration in the mechanical properties. The interface monitoring can give the relationship between % moisture absorbed and the effect on the glass transition temperature.

7.REFERENCES

1. **Metals Handbook disk Edition Ed**, J.R. Davis, *ASM International, Materials Park, Ohio*, pg 39.

2. B.Z. Jang, **Advanced Polymer Composites: Principles and Applications**, *ASM International*, OH, 1994, pg 3.

3. N.K. Naik et al, **Hybrid composites under high strain rate compression loading**, *material science and engineering*, vol 498, issue 1-2, 2008, pp 87-89.

4. N.L.Hancox, T**he environmental response of hybrid composites**, *journal of mat sci*, vol 19, 1984, pp 1969-1979.

5. L.Oval, **Effect of stacking sequence on the mechanical properties of glass-carbon hybrid composies before and after impact**, *journal of industrial textiles*, vol 31, no 4, 2002, pp 255-271.

6. B.Z. Jang, **Advanced Polymer Composites: Principles and Applications**, *ASM International*, OH, 1994, pg 22.

7. T.Hayashi, *8th reinforced plastics conference*, uk, 1972, pp 149.

8. T.Hayashi, *8th reinforced plastics conference*: G**lass fibers**.

9. J.B.Donnet, **Carbon fibers**, N.Y.International fiber sci&tech, 1984.

10. W.D.Callister, M*at sci & engg*, An introduction, asia, john wiley and sons, 2001.

11. **Metals Handbook disk Edition Ed**, J.R. Davis*,* ASM International, Materials Park, Ohio, pg 71.

12. A. Kelly, C**omprehensive composite materials, Polymer matrix composites**, oxford, uk, *Elsevier science pub*, 2000.

13. **Composite materials and applications**, Daniel Gay et al, crc publications, Washington D.C, 2003, pg 146.

14. D.Hull, T.W.Dyne, **An introduction to composite materials**, Cambridge,U.K: *Cambridge university press*, 1996.

15. **Composite materials and applications**, Daniel Gay et al, crc publications, Washington D.C, 2003, pg 23.

16. B.C.Ray, **Adhesion of glass/epoxy composites influenced by thermal and cryogenic environm**ents, J*ournal of applied polymers science*, vol 102, no2, 2006, pp1943-1949.

17. N.L.Hancox, **The environmental response of hybrid composites**, *journal of mat sci*, vol 19, 1984, pp 1969-1979.

18. B.C.Ray, **Hygrothermal effects on the mechanical behavior of fiber reinforced polymeric composite,** *metals materials and processes*, vol 3, no 2, pp 99-108.

19. A.K.Munjal, **In advanced composites**, conf. proc., 2-4 dec 1985, *American society of metals*, 1985, pp 309-321.

20. D.E.Pettit, K.N.Lauratis, and J.M. Cox, AFWAL-TR- 79-3095, vol 1, 2 and 3, *Air force wright aeronautical laboratories*, 1979.

21. B.C.Ray, Loading **Rate Sensitivity of Glass Fiber-epoxy Composite at Ambient and Sub-ambient Temperatures**, *Journal of Reinforced Plastics and Composites*, Vol 25, Iss 3, 2006, P 329-333.

22. B.C. Ray, **Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites**, *Journal of Colloid and Interface Science*, 298 (2006) 111–117.

23. B.C.Ray, **Assessment of small interactions and structural gradient at the interface of glass and carbon fibers epoxy micro-composites by FTIR-imaging and DSC techniques,** 2007.

24. B.C.Ray, **Loading Rate Sensitivity of Jute/Glass Hybrid Reinforced Epoxy Composites: Effect of Surface Modifications**, *Journal of Reinforced Plastics and Composites,* Vol. 26, No. 9, 851-860 (2007).