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Title of Contribution

**Mechanical behavior of polymer composites at cryogenic temperatures**

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Abstract: High strength, stiffness and low weight remain the winning combination that propels composite materials into new arenas, but other properties are equally important. It offers good vibrational damping and low coefficient of thermal expansion (CTE), characteristics that can be engineered for specialized applications. Commercial composites used in large markets such as, automotive components, boats, consumer goods and corrosion-resistant industrial parts. Advanced composites, initially developed for the military aerospace market offer performance superior to that of conventional structural metals and now find applications in satellites, aircraft, sporting goods and in the energy sector in oil and gas exploration and wind turbine construction.

Cryogenic applications of polymeric fiber composites are mainly in super conductivity, space technology and handling of liquefied gases. On contrast, heterogeneous nature and anisotropic behaviour of FRP’s, a structural designer is faced challenge in predicting the integrity and durability of FRP laminates. Severe environmental exposure affects physical and mechanical properties of polymeric composite materials resulting in an undesirable degradation.

Polymer composites soften, creep and distort when heated to high temperature (>100°C) is accompanied by collapse of free volume as the molecular adjustment takes place, that can result in buckling and failure of load-bearing composites structures. Cryogenic fuel tank is the most structural application of FRP at low temperature. Expose to this cryogenic temperature can cause microcracks as well as delamination in the composites due to thermal residual stresses. These microcracks provide a pathway for the ingress of moisture or corrosive chemicals and possible pathway for loss of cryogenic fluids in the tanks. Matrix resins at low temperature are brittle manner and do not allow relaxation of residual stresses or stress concentration to take place. At low temperatures polymers are well below their glass transition temperature and show little visco-elastic behaviour. Molecular motion of segments or side groups is still possible, but
the degrees of freedom decrease with decreasing temperature. This motion influences the damping behaviour of the polymers under cyclic mechanical load. If the temperature dependent relaxation time of molecular motion is equal to the time of external deformation, maximum power dissipation occurs. Simultaneously a change in the shear modulus is observed. The goal of this chapter is to extensively study on the in-plane mechanical properties of FRP composites at cryogenic temperature. The composites which have been considered include carbon, glass and Kevlar fiber-reinforced polymers with different resin matrix.

**Key words:** Polymer matrix composite, Cryogenic temperature, Failure and fracture, Scanning electron microscope, Interphase, Atomic force microscope, Alternating differential scanning calorimeter
Contents

4.1 Introduction
4.1.1 Status and Strength
4.1.2 Prospects and problems
4.2 Architecture and character of synthetic fibers and chemistry of matrix resins
4.2.1 Glass fiber
4.2.2 Carbon fiber
4.2.3 Kevlar fiber
4.2.4 Unsaturated Polyester
4.2.5 Vinyl Ester
4.2.6 Epoxy Resin
4.3 Molecular motion and relaxation behavior of matrix resins
4.3.1 Relaxation behavior and Glass transition (Tg)
4.3.2 Effect of a mechanical action on Tg
4.3.3 Viscoelasticity (elastomer) behavior at low temperature
4.4 Mechanical properties of FRP composites at low temperature
4.4.1 Deformation characteristic of FRP at different temperatures
4.4.2 Implication of hygrothermal environments on failures
4.4.3 Loading rate sensitivity of FRPs at low temperatures
4.4.4 Status of interfaces on mechanical behavior
4.4.5 Failure revelations through microscope and microanalysis
4.5 Possible Failure modes of FRP composites at low temperatures (Energy- absorbing mechanisms): Micromechanics and Progressive failure
4.5.1 Matrix deformation and cracking
4.5.2 Inter fiber fracture (IFF) and Fiber pull-out
4.5.3 Delamination
4.5.4 Interfacial damage and debonding
4.6 Some issues in the interface, matrix and fibers of FRP composites at low temperature
4.6.1 Experimental explorations

Reasonable remarks
Acknowledgements
References

Abbreviations
FRP Fibrous Reinforced Plastic
GFRP Glass fiber reinforced plastic
CFRP Carbon fiber reinforced plastic
ILSS Interlaminar shear strength
FTIR Fourier transforms infrared spectroscope
TMDSC Temperature modulated differential scanning calorimeter
AFM Atomic force microscope
SEM Scanning Electron microscope
IPN Interpenetrating network
Tg Glass transition temperature
PMC Polymer matrix composites
4.1 Introduction

4.1.1 Status and Strength

Last many decades composite material be endowed with an interesting topic to all engineers and manufacturers. The first appearance of composites dates back to the 1500s B.C. when Mesopotamians and Egyptians settlers made their strong and long durable home with a mixture of mud and straw. Straw acts as reinforcement and fulfill all the optimum properties. In the board class of composites the major categories are; metal matrix composite (MMC), ceramic matrix composite (CMC) and polymer matrix composite (PMC). The canon following the materials applications and degradation are very specific to the composite material. Above all, the current chapter focuses mostly on polymer matrix composites especially emphasizes on prospect and performance at low temperatures.

The term *composite* stipulate a very broad class of materials, made of several(at least two) components. By opposition to alloys, the composite constituents are generally distinct at the macroscopic level. However, composite materials are often engineered to answer specific requirements. Commercial composites used in large markets such as, automotive components, boats, consumer goods and corrosion-resistance industrial parts. Advanced composites, initially developed for the military aerospace marked offer performance superior to that of conventional structural metals and now find applications in satellites, aircraft, sporting goods and in the energy sector in oil and gas exploration and wind turbine construction. According to Luedtke, aircraft doors, fairings and interior panels are perfect for the FRP technology. Other potential applications could include the horizontal tail leading edge, pylon stub fairing and engine cowl panel troop door deflector (Stanley 2003). Largest aircraft the Airbus A380 have eleven times greater than the length and over 1000 times the weight of the Wright’s 1903 Flyer, this super-jumbo will
be the first airliner to have carbon fiber composite centre-wing box. Besides that the rear pressure bulk-head, critical to passenger safety, will be of CFRP, as will the entire rear fuselage aft of the bulkhead. This is one of the largest carbon fiber parts yet produced by Airbus. The composite A500 carbon Aero from Adam Aircraft has now flown successfully in mid 2003. In helicopter, the use of composites material in several critical applications as Boeing-Sikorsky Comanche helicopter and Bell-Boeing V22 Osprey tiltrotor. The parts including exhaust doors, shrouds for transmission and tail rotor blades. That’s why the composite deck is expected to last for more than 50 years with little to no maintenance.Currently employed to manufactures a family car where the metal bumpers, radiator end tanks, door handles and front and rear ends are substituted by engineering plastics (Dorgham 1986; Wood 1991). World’s oldest composite industry was found in Russia. Looking upon the future of this, Russians are fighting against few constrains of the gravity with the composite applications and there are some exploring opportunities are available. Russia has a very comprehensive large distance rail road network and major cities underground transport systems. As more and more cargo and people travel by rail, there is strong need for refurbishing the rolling stock. The coaches and wagons are very cold in temperature and face severe corrosion problems. It seems that composites material now the best choice for the refurbish old system(Gauffin 2005)A recent example is the Bridge-in-a-Backpack for 2014 Winter Olympics in Russia, an innovative inflatable composite-concrete arch bridge, which was developed to reduce construction time and costs, increase lifespan, reduce maintenance costs and reduce the carbon footprint of bridge construction. Polymer matrix key to an emerging breed of racing powerboats (V24) designed to make sport accessible. Here the hull bottom is stepped in two places to minimize wetted area as the boat rises in the water at speed and to help aerate the water’s surface layer, so providing a more forgiving ride (Marsh 2004). Windmill blades made of
FRP are exposed to a large number of sustained and occasional environmental loads such as bending, vibrations, UV, cold and heat, moisture and also impact loading. Such loads combined with large dimensions perfectly illustrate the challenge of durability assessment of composite materials.

The fibrous polymeric composites at cryogenic temperature undergo inelastic deformation and damage when it subjected to mechanical loading. Despite such a restriction, the field of polymer composites still remains broad. Indeed, the nature and geometry of the materials constituents define to a large extent the response of the composite to external mechanical and environmental loads. At low temperature, the material might have some nucleating cracks and delaminated areas possibly by misfit strains at the interface region due to difference in coefficient of thermal expansion. In other aspect, matrix resin behaves brittle at low temperature unless it is modified by other modifier agent to increase its toughness value and retaining its strain capabilities. However, at low temperature the performance of fiber is not well-evaluated and critically characterized. Unless and until a complete and comprehensive understanding about the constituents (fiber, matrix resin and interphase) of FRP composites is being assessed and explored, the full potential of these material may not be fully utilized at cryogenic applications.

4.1.2 Prospects and Problems

Structures like the ‘Benghazi dome’ an advanced roof of Dubai Airport, and the roof of London’s Covent Garden flower market testify the long term durability and integrity of composite structure. A GFRP reinforced church spire erected near Birmingham, UK, in 1961 was found still to be in service. Many instances where composites have been employed so far, they add,
have been pilot or demonstration projects, where better than average care may have been taken about their design and implementation. Boeing has awarded a project for developing design damage tolerance. A marine engineer would go about designing a propeller, where plastics could be found strong enough to serve the required purpose. Many ships have propellers made of metals which is corroded easily in sea water and set up galvanic action. To overcome these problems, plastics play a vital role. Resin systems Edmonton, Canada is launching a range of composite hockey stick shaft which is urethane based composite resins with fiber replacement technology. This type of hockey stick has better cut resistance, impact resistance as compared to other competitive products. Most polymer matrices are characterized by the presence of amorphous phases. Due to this nonequilibrium state, polymer composites are particularly sensitive to environmental factors such as temperature, time, and exposure to liquids, gases, electrical fields and radiation. Static and dynamic mechanical loads can interact with the environmental parameters and accelerate the degradation process. Defects along the matrix and reinforcement interface further amplify the action of environmental factors. In this book, we propose to investigate the effects of the low temperature on the structural integrity of polymer matrix composite.

Hydrogen technology is rapidly progressing. Liquid hydrogen vessels for vehicles will be built with lightweight materials of high specific strength and fatigue resistance and low thermal conductivity. Wind tunnels yield much higher Reynolds numbers when operated at cryogenic temperature. Carbon fiber composites (CFRP) are the prime candidate which has a high specific strength and a high fatigue endurance limit for this application. The continually expanding use of FRP composites in large structural applications requires a better understanding of the interdependent thermal and mechanical responses of the FRP when it is subjected to elevated and high temperatures. The thermo-mechanical behavior of FRP composites depends mainly on that of the polymer resin
For worthier application of fibrous composite a comprehensive understanding of the mechanisms of ageing and environmental degradation is of immense importance. Environmental attack can degrade fiber/matrix interface mostly by mechanochemical principle. Thermal aging behavior of epoxy resins is of special interest because of their expanding use for structural applications where increased temperatures are common environmental conditions (Senussi et al. 1989). A material that exhibits ductile behavior at room temperature may become brittle at low temperatures or may soften and creep at elevated temperatures (Jang 1994). With these temperature fluctuations changes in strength and or stiffness are observed as well. The effect of the combination of thermal and mechanical stresses may well cause a change in mode and location of failure as well as a change in threshold load factor needed to cause failure. It is very difficult to generalize the effect of change of temperature. The matrix dominated properties are such as compressive, flexural, shear and transverse properties are most affected by the temperature dependence on the matrix. Thermal conditioning imparts better adhesion and thus, an improved ILSS value especially at the less conditioning time (Shindo et al 2011). When considering the temperature dependence for the physical properties of many polymeric materials, various relaxation effects are extremely important. Thermal degradation of resin involves chemical reaction and physical changes. Chemical reaction is represented by oxidation, further cross-linking and further reaction of un-reacted monomers, while physical change is the visco-elastic behavior. The visco-elastic yield behavior generally depends upon the temperature and loading rate. At the macromolecular scale chain scission and cross-linking affect the polymer network and thus, alter the mechanical properties of the oxidized layer (Hartwig 2004). At the macroscopic level, the hindered shrinkage of the oxidized layer induces a stress gradient susceptible to initiate and propagate cracks (Lee 1993). Thermal conditioning behavior of glass/epoxy and carbon/epoxy composites is of special
interest, because of their expanding use for structural applications, where increased temperatures are common environmental conditions. Fracture processes of polymers are strongly influenced by deformation or yielding processes which depend on temperature and time. At very low temperature no yielding is possible and fracture is brittle. At high temperatures two characteristic phenomena occur after the yield point: strain softening and strain hardening (Hartwig 2004). The specimens tested at a lower temperature are characterized by a greater level of micro-cracking and de-lamination. These effects are believed due to higher thermal residual stresses. Due to heterogeneous nature of the fiber and matrix there is larger thermal expansion and contraction mismatch which generates thermal stresses. This weakens the fiber/matrix interface as a result their interlaminar shear strength (ILSS) values deteriorate progressively.

4.2 Architecture and character of synthetic fibers and chemistry of matrix resins

A large choice of synthetic fibers is available at present to tailor the FRPs to meet the needs of a wide spectrum of applications starting from casual to super-critical range. Glass, carbon and Kevlar fibers represent the major classes of reinforcement for advanced composites. Glass is an amorphous material (i.e. non-equilibrium) in nature. Glass has been used for various purposes since thousands of years. Different grades of Glass fibers: E-glass (E for electrical) is based on CaO-Al₂O₃-SiO₂. Its excellent processability enables the drawing of long fibers for relatively low costs. S-glass on the other hand is based on SiO₂-Al₂O₃-Mg and exhibits a higher stiffness and strength. Unfortunately, the higher temperature resistance of S-glass also translates in more difficult fiber manufacturing processes, yielding higher fabrication costs. Carbon fibers are generally used for more advanced applications. Carbon fibers can be developed from different precursors such as rayon, cellulose and polyacrylonitrile (PAN). Manufacturing processes are generally complex and details kept proprietary. The price of carbon fibers still remains high and their use
is generally confined to key components where the high stiffness to weight ration enables significant cost reductions. For calculation purposes especially, it might also be meaningful to classify composites with respect to their reinforcement geometries. Multiple reinforcement geometries exist including continuous fiber reinforcement, fabrics, short (mat) reinforcement, particulate reinforcement and occasionally three-dimensional reinforcement. Depending on the application, such reinforcements can be included in various composite structures such as single layers, laminated structures, or sandwich composites.

Aramid fiber is used to make a variety of clothing, accessories, and equipment safe and cut resistant. It’s lightweight and extraordinarily strong, with five times the strength of steel on an equal-weight basis. Best known for its use in ballistic and stab-resistant body armor, Kevlar® brand aramid fiber has shown its own heroism in helping to save the lives of thousands of people around the world.

4.2.1 Glass fiber
Glass fibers have wide applications in all sector of polymer composite. It used to make aircraft, marine, civil infrastructure, sporting goods (Kelly 2000; Bunsell et al 2005; Kaw 2006; Hull 1981). A well known application is hull of yachts. This is ideal use for fabric with polyester resin and glass fiber. In marine environment which is freedom from corrosion. The nonmagnetic nature of glass fiber is an excellent choice for minesweeper hulls, instead of magnetic steel put them at a disadvantage. During World War I, glass fibers (replacement for asbestos) from Germany by touching a heat-softened glass rod to a spinning wheel (Moncrieff 1979).
**Structure and properties of glass fiber**

After World War II, the fibers take the market in a great volume for reinforcement with polymer. Various types of glass fiber exist, but the chemical position mostly based on silica (SiO$_2$) with addition of oxide of alumina, sodium, magnesium, calcium. This can be produced in either continuous filament or staple form. The molten glass extruding through hole of diameter is of 1 or 2 mm in a spinner jet. This fiber diameter usually lies between 5 to 15 μm. The fiber diameter greatly influenced by, the winding speed and viscosity of molten glass. Compositions of E-glass fiber are SiO$_2$-52.4%, Al$_2$O$_3$-14.4, CaO- 17.5, MgO- 4.5 and B$_2$O$_3$-8.0 in different weight percentages (Hull. D 1981).

![Fig 4.1: Two-dimensional polyhedron network structure of sodium silicate glass. (Hull D 1981)](image)

The important features of glass fiber reinforced polymer composite are good corrosion resistance, lightweight, high toughness, high absolute and specific strength values, process and shape freedom. From micromechanics point of view the glass fiber transfer the load from fiber to fiber properly, the selection of matrix resin is a crucial point (Thomson 1995).

In response to the numerous and diverse range of GFRP, thermosetting polymer resin are more reliable. Generally high strength curing systems are more durable and environment friendly.

**Silane treatment of glass fibers**
From last 3 decades, glass fibers play a dominant role for various composite applications. It is partly indebted to the development of silane coupling agents. It acts as a protective layer for glass fibers and act as a coupling agent to endorse adhesion with the polymer matrix resin. The polyhedron network structure of sodium silicate glass schematically shows, each polyhedron can be seen to be a combination of oxygen atoms around silicon atom bonded together by covalent bonds (Plonka 2004). The sodium ions are linked with charged oxygen atoms by ionic bonds but not linked to network. This 3D network of glass exhibits isotropic properties. In case of carbon and Kevlar which are shows anisotropic properties. The unique characteristic of glass fiber is that the elastic modulus along the fiber axis is same as that of transverse direction (Jang 1994). The physical and mechanical properties of glass fiber are Diameter (μm)-5-25, Density- 2.54, Elastic modulus at 25°,kg/mm²- 7700, Tensile strength (GPa)- 2.4, Young’s modulus(GPa) -72.4, Coefficient of thermal expansion 10⁻⁶°C- 5 (Hull 1981).

To explain the interfacial bonding mechanisms of silane coupling agents with the fiber surface several theories are proposed. Chemical bonding is widely spread (Watts 1980; Kim et al. 1992). Silane mostly containing organofunctional groups for different resins chemistry. The structure of oraganosilanes is X₃-Si-R. This acts as a siloxane bridge between the resin and the glass fiber by forming a chemical bond. This multifunctional molecule, react at one end with the glass fiber surface and the other end with polymer surface. The R group generally reacts with the matrix resin and X is group which can hydrolyze to form a silanol group in an aqueous solution and react with hydroxyl group of the glass surface.
The thickness and orientation of the fiber are determined by conditions of deposition, topography of glass fiber surface, concentration of solution and length of the treatment duration (Ishida et al. 1980).

The microstructure of coupling agent depends upon various factors. The coupling agent-resin matrix interface is a diffusion boundary where intermixing takes place, due to penetration of the resin into the chemisorbed silanes layers and the migration of the physisorbed silane molecules into the matrix phase (Moussawi et al. 1993). The interphase material tends to have a lower glass transition temperature (Tg) higher modulus and tensile strength and lower fracture toughness than the bulk matrix (Kim and Mai 1998).

Apart from mechanical property, the characteristic of silane treatment is its ability to provide the glass fiber with a water resistance bond. The degradation of untreated glass fiber-resin matrix interface is more affected by water. The water penetrates into the interface region by diffusion along the fibers which is eventually absorbed by the glass fiber. The water molecules formed weak hydrogen bond with the oxides groups of glass fiber. It hydrolyze the existing bond and then weak the adhesion level, which tends to degrade the mechanical properties (Kim and Mai 1998).

The glass fiber shows four different types of fracture surfaces. These regions include as: a smooth mirror region, a mist region with some radial ridges, a hackle region consisting of big ridges and finally branching of crack propagation.
Silane agents are intended to act as a protective coating for glass fiber surface and a coupling agent to promote the adhesion with the polymer matrix. The silane agents are applied to glass fiber surface as a size along with other components. Use of silane coupling agent for improving the bond quality and a wide variety of organofunctional silanes has been developed. In the chemical bonding theory, the bifunctional silane molecules act as a link between the resin and the glass by forming a chemical bond with the surface of the glass through a siloxane bridge, while its functional groups bond to the polymer resin. The general chemical formula is shown as XaSi-R, multi-functional molecules that react at one end with the glass fiber surface and the other end with the polymer phase. R is a group which can react with the resin, and X is a group which can hydrolyze to form a silanol group in aqueous solution (Fig. 4.2) and thus react with a hydroxyl group of the glass surface. The R-group may be vinyl, ~,-aminopropyl, ~,- methacryloxypropyl, etc.; the X-group may be chloro, methoxy, ethoxy, etc.

**Fig 4.2:** Functions of coupling agents, a) Hydrolysis of organosilanes to corresponding silanol. b) Hydrogen bonding between hydroxyl group of silanol and glass surface. c) Polysiloxane bonded to glass surface. d) Organo functional R-group reacted with polymer.
The subject of silane chemistry and its interaction with both glass surface and polymer resin have been studied extensively.

Regarding this there is some factors are related with this statement…

a) The chemical reactivity of the organofunctional group of the silane to form covalent bonds with the polymer matrix,

b) The primary or secondary chemical bond formation at the glass interface

b) And the ability of the polymer matrix to diffuse into the siloxane interphase to form a rigid, tough, water resistant interpenetrating polymer network as a transition zone between the bulk matrix and the glass reinforcement (Ishida and Koenig 1979).

**Interpenetrating polymer network: (IPN)**

A layer of silane agent usually does not produce an optimum mechanical strength and there must be other important mechanism taking place at the interface region.

![Fig 4.3](image)

**Fig 4.3:** A schematic model for interdiffusion and inter-penetrating network in a silane treated glass fiber-polymer matrix composite. (Plueddemann et al 1980).

However, the presence of a stiff fiber mitigates the effect of a soft interphase, increasing the effective modulus of the interphase beyond that of the bulk matrix in close vicinity of the fiber (Plueddemann 1974; Plueddemann et al1980). As stated above, FTIR and other spectroscopic techniques were used to quantify the rates of interdiffusion and chemical reaction between si-
lanes and polymeric matrices. Generally it may conclude that the formation of interpenetrating networks contributed to increase in interfacial adhesion and that the conditions under which the silanes were applied had a significant effect on the mechanical properties of the resulting composites (Williams et al 1990; Tsai et al 1990).

4.2.2 Carbon fiber

Carbon fibers are a significant volume fraction of modern structural airframes. Embedded into polymer matrices, they provide significant strength and stiffness gains by unit weight compared with competing structural materials (Frank 2011). Last few decades vast improvements in the carbon fibers have been obtained. In larger part, these improvements were accelerated in the field of aerospace, space and various industries in response to higher strain-to-failure fibers. Higher strain, higher modulus carbon fibers are merging with the resin matrix to provide optimum properties i.e. load-bearing capacity in various applications.

This evolving fiber manufactured by organic fibers (precursors) by treating it heat to have the order carbon structure. The precursor mainly polyacrylonitrile (PAN) and pitch (Jang 1994). Scanning Tunnelling microscopy (STM) reveals systematic change in surface profile as a function of oxidative fiber surface treatment. The topography of PAN based carbon fiber consists of graphitic platelets of dimensions 30 ×20×100 nm. The adhesion between fiber and matrix is a function of surface treatment. If the concentration of oxidation is more there is decline of interfacial bond strength (Marshal and Price 1991).
PAN based fiber fell into different sections: a) high strength b) high modulus c) ultra high modulus (Pepper et al. 1983). Polyacrylonitrile (PAN) is a long-chain linear polymer composed of a carbon back bone with attached carbonitrile group. While treating this fiber in an oxidizing atmosphere at temperature in the range of 200 to 300°C, we obtain carbon fiber.

**Table 4.3:** Types carbon fibers

<table>
<thead>
<tr>
<th>Carbon (%)</th>
<th>Fiber property</th>
<th>Heat treatment temperature(°C)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>92-96</td>
<td>High strength</td>
<td>1200-1400</td>
<td>228-241</td>
</tr>
<tr>
<td>92-96</td>
<td>Intermediate modulus</td>
<td>~1400</td>
<td>290-310</td>
</tr>
<tr>
<td>99</td>
<td>High modulus</td>
<td>1800-2500</td>
<td>276-380</td>
</tr>
<tr>
<td>99^</td>
<td>Ultra high modulus</td>
<td>2800-3000</td>
<td>483-690</td>
</tr>
</tbody>
</table>

**Table 4.4:** Properties of PAN based carbon fiber

<table>
<thead>
<tr>
<th>Property</th>
<th>High strength</th>
<th>Intermediate modulus</th>
<th>High modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength,MPa</td>
<td>2300</td>
<td>2600</td>
<td>1420</td>
</tr>
<tr>
<td>Tensile modulus,GPa</td>
<td>145</td>
<td>180</td>
<td>210-250</td>
</tr>
<tr>
<td>Compression strength,MPa</td>
<td>1600</td>
<td>1800</td>
<td>900</td>
</tr>
<tr>
<td>Compression modulus,GPa</td>
<td>135</td>
<td>150</td>
<td>190-230</td>
</tr>
<tr>
<td>Short beam shear stress, MPa</td>
<td>120</td>
<td>120</td>
<td>80</td>
</tr>
<tr>
<td>----------------------------</td>
<td>-----</td>
<td>-----</td>
<td>----</td>
</tr>
</tbody>
</table>

The strength of carbon fiber depends on the type of the precursor fiber used. Its treatment temperature along with presence of flaws or defects has a great impact on the durability of the fiber (Donnet et al 1984). With increasing heat treatment temperature at about 1000°C the strength was increased (Thome 1970; Jones 1971).

**Surface treatments of carbon fibers**

The poor shear strength of carbon fiber reinforced polymers, those reinforced with high modulus fibers in particular, in generally attributed to a lack of bonding at the fiber/matrix interface. The mechanism of bonding between carbon fibers and polymer matrices are as complex as that of glass fibers, and there are more complications associated with the carbon fiber surface because it is highly active and readily absorbs gases. A schematic model for chemical reaction between oxidized fibers and epoxy resin is presented:

![Schematic models for chemical reaction between oxidized carbon fiber surface and epoxy matrix](Fig 4.5: Schematic models for chemical reaction between oxidized carbon fiber surface and epoxy matrix (Horie et al 1977))

The mechanism of chemical bonding due to the presence of functional groups, change the energetic of the carbon fiber surface considerably. However, there must be a limit to the improvement in bond strength by surface treatment only. A decrease in bond strength and other deteri-
orating effects are exposed to occur if the surface treatment is excessive, leading to severe damage of the fiber.

**Surface treatment on composite properties**
The interlaminar shear strength (ILSS) flexural and tensile strengths are increased as the principal effects of fiber surface treatment on composite properties. The enhancement of these strength properties depend on the fiber elastic modulus, the degree of surface treatment and the type of resin and curing agent used. The largest improvement in ILSS is obtained for high modulus fibers. Enhancement of the interfacial bond strength changes the failure mode from "interface-dominated" to matrix-dominated", which is mainly responsible for the increase in interlaminar fracture toughness.

![Fig 4.6](image)

**Fig 4.6:** Effect of carbon fiber surface treatment on ILSS and impact energy for a carbon fiber-epoxy matrix composite. (Goan et al. 1973)

The longitudinal tensile strength of the composite is found to increase with interfacial bond shear strength. When the interface bond strength is very high, the failure location changes from the interface to the surrounding matrix and the composite become brittle. With increasing interface bond strength, the compressive strength is also enhanced to a greater extent than the tensile strength.

**4.2.3 Aramid fiber**
This fiber is a generic term of aromatic polyamide fibers with 85% of the amide linkage are linked directly to two aromatic rings (Takayose et al 1982; Chiao 1977). At the present stage and in the future, the principle aramid fiber for composite reinforcement for high performance composite will be Kevlar. It is available in four categories: Kevlar, Kevlar 29, Kevlar 49, and Kevlar 149. More recently, DuPont Kevlar AP is the next-generation fiber that put forth for advanced performance of composite material. It increases the design flexibility and durability of various structures. DuPont Kevlar K29 AP and Kevlar K49 AP are the future prospects fibers to become commercially available. Due to high strength, stiffness and low density the fibers has vast used in aerospace composite, aircraft, military. Besides that the longitudinal failure mode of fiber is more applicable for ballistic resistance of composite material.

An increasing use of Kevlar fibers is in low thermal expansion composite circuit boards, which leads to negative coefficient of thermal expansion. The strong covalent bonds in the fiber axis direction provide high longitudinal strength, where as the weak hydrogen bonds in the transverse direction results in low transverse strength.

**Surface chemistry**
Aramid fibers exhibit skin and core structure with distinct physical properties. The surface consists of an oxidized hydrocarbon with approximately twice the oxygen content and half of the N content of the bulk. Kevlar 49 exhibits higher surface oxygen content than Kevlar 29. With the help of XPS it is observed that, oxide primarily consists of hydroxyl and ether linkages with similar amount of carboxyl and carbonyl groups (Allred et al 1985; 1984). The thickness of the oxide layer is of the order of 20Å. From morphological point of view, the fiber consists of extended –chain, which are highly oriented in the fiber direction. Hydrogen bonded sheets of these chains exists in the latest fiber direction (Northolt 1974).
Table 4.5 XPS surface composition of Aramid

<table>
<thead>
<tr>
<th>Aramid</th>
<th>Composition (carbon)</th>
<th>Oxygen</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 29 yarn</td>
<td>70</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Kevlar 49 yarn</td>
<td>68</td>
<td>25</td>
<td>7</td>
</tr>
<tr>
<td>Kevlar 49 Fabric</td>
<td>73</td>
<td>22</td>
<td>5</td>
</tr>
</tbody>
</table>

Fig 4.7: Schematic presentation of Kevlar 49 aramid fiber

Properties of Kevlar fiber at 23°C are tensile strength (MPa) - 3024, tensile elongation (%) - 2.48

Table 4.6 Properties of Kevlar 49 at 23°C (Lee 1993)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>3024</td>
</tr>
<tr>
<td>Tensile elongation (%)</td>
<td>2.48</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>121.9</td>
</tr>
<tr>
<td>Tensile strain, %</td>
<td>2.5</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, 10^-6°C</td>
<td>-2.0 (Kevlar 29)</td>
</tr>
</tbody>
</table>

When Kevlar 49 fibers are placed compression along the longitudinal axis, they buckle and form kink-bands. Both the weak lateral H-bonding of Kevlar 49 fibers and the presence of residual impurities in the interfibrillar regions contribute to the buckling susceptibility of the fiber. Kevlar 49 epoxy composite fail in tension by axially splitting 20 to 50 times the diameter of the fiber along their length (Lee et al. 1988). Depending upon temperature, Kevlar fiber loss its me-
mechanical properties with increasing temperature but at low temperature it is essentially no loss in mechanical properties (DuPont 1983). At 200°C, there is a 20% loss in strength modulus and 25-40% loss in tensile strength (Morgan et al. 1980; Smith 1980).

**Environmental liability**
Kevlar 49 are hygroscopic in nature and can sorbs up to 3.5-4.5 wt % in ambient temperature at 100% relative humidity (Penn 1979). Moisture sorption from humid air occurs rapidly. Equilibrium moisture content is attained in 16-36 hr (Moss 1978). At ambient temperature no swellings observe in Kevlar fiber when moisture absorb for long time duration. But above 100°C the superheat steam is the prime reason for the permanent structural damage, which leads to 10 wt % moisture gain (Morgan 1984). The unique chemistry and morphology of Kevlar polyaramid is also manifested in composite behavior. It was assumed the adhesion strength between Kevlar fiber and epoxy is excellent due to intermolecular forces and the covalent bond exists between the Kevlar fiber and the matrix region.

### 4.2.4 Unsaturated polyesters
Unsaturated polyesters are very unique polymer for the polymer fiber reinforced polymer composites. The good balance between mechanical properties and chemical resistance is required at room and moderate temperature. It shows high shrinkage on curing and absorbs water under certain conditions. These polymers are made by a reaction of glycol such as propylene glycol with an unsaturated acid and cross-linking the resulting polymer with unsaturated monomer. Water is formed as a condensation type while reaction is occurred and it should be removed. This polyester alkyd is blended with styrene monomer in the ratio of about 2 parts alkyd and 1 part styrene mixture. The poor impact resistance, limited shelf life and high curing shrinkage make the polymer utilization for high performance of applications. The notable area of application for
fibrous polyesters includes appliances business equipment, sporting goods, construction and transportation. In contrast polyester resins unlike other undergo net shrinkage after long exposure to water (Updegraff 1982). Three processes (hydrolysis, hydrophilisation formation and migration of low-molecular weight electrolytes) predominate at different stages of water sorption behavior in composites. It was observed that it is more susceptible to damage/debonding by thermal fatigue compared to epoxy resin matrix composites (Ray 2005; Camino 1997).

4.2.5 Vinyl ester
Vinyl ester is the mixture of unsaturated carboxylic acids to epoxide resin. The C=C double bond formed only at the end of vinyl ester molecule due to this cross-linking takes place. This is made by mixture of unsaturated carboxylic acids and epoxide resin (Launikitis 1982). Due to less cross-links, it is more flexible and have high toughness than polyester resin. The volume shrinkage (5 to 10%) of vinyl ester resins, although lower than that of polyester resins and higher than the epoxy resin. It can be used in polymer composite as pipes, storage tank, scrubbers.

Fig 4.8: Preparation of vinyl ester resin
Last few decades high quality fiberglass vinyl ester swimming pool, first manufactured in United State. However, vinyl ester is more sensitive to moisture, temperature and mix ratio (with cata-
lyst). Due to low ester content and low vinyl functionality it has greater resistance to hydrolysis, therefore preferred in applications requiring chemical resistance (Bascom et al. 1987).

**4.2.6 Epoxy Resins**

Epoxy resins are the most common material for high performance advanced fibrous polymeric composites, but they are inherently brittle because of their high degree of cross linking. The densely cross linked structure are the basis of superior mechanical properties such as high modulus, high fracture strength, solvent resistance. However these materials are irreversibly damaged by high stress due to the formation and propagation of cracks. At cryogenic temperature the mechanical properties of polymer composite is influenced by matrix failure or propagation of microcracks. This is nucleated by the residual stress and strain in the matrix resin system. At low temperature the matrix becomes stiffer and stronger but less ductile (brittleness is high). In alliance with very less or negative CTE fibers, more and more residual stresses are generated on the matrix region. Because of this few free stress and strain are accessible for the external loading of composite material at cryogenic temperature. The low temperature shear strength of epoxy resins lies between 150 and 200 MPa at T<77K (Hartwig 1984). The most important epoxy resins are characterized by the existence of the epoxy group, which is a three member ring with ring with two carbons and an oxygen atom.

![Epoxy Resin Structure](image)

**Fig 4.9:** Preparation of epoxy resin

Diglycidyl ethers of Bisphenol are the most widely used epoxy resin. Epoxy resin is the three membered ring with one oxygen and two carbons. This epoxy group is helpful for the adhesion of reinforcement surface which increases the strength and durability of composite material. It
found enormous application as adhesives, bonding and as sealants. These resins easily react with epoxies and have good thermal stability and greater cross-linking density.

**Fig 4.10:** Curing of epoxy resin

Usually epoxy resins are used in conjunction with a curing agent to reduce curing time and to activate desirable properties. Aerospace applications require high toughened epoxy resin to impart damage tolerance and necessary interlaminar fracture toughness. It is more expensive than polyester resins but it is not so much suitable for elevated temperature use.

**Low Temperature Physics of Reinforcement Fibers, Matrix Resins and interphase region**

Composite technology is based on taking advantage of the stiffness and strength of high performance fibers by dispersing them in a matrix, which acts as a binder, and also transfers forces to the fibers across the fiber-matrix interface. Severe environmental exposure affects physical and mechanical properties of polymeric composite materials resulting in an undesirable degradation. As the material is intrinsically heterogeneous, damage and degradation in material will therefore often be strongly influenced by local processes. The anisotropy contributes to more complexity in the assessment of the damage mechanisms and in their impact on the composite responses. Molecular motion of polymer matrix at low temperature will be abysmal; molecular motion will be small and re-orientation modes will be relatively simple. Many of the amorphous polymers exhibited cryogenic relaxation peaks which determined by intermolecular forces (Hiltner 1974).
At low temperature the intrinsic conductivity tensor of carbon fibers becomes more isotropic. This is due to only long-wave phonons are activated which propagate in a similar mode as in transverse and longitudinal directions of graphitized areas. In case of Kevlar fiber, the mean transverse stiffness is similar to that of isotropic polymer matrix resin at low temperature.

The deportment of interface region at low temperature: glass fiber contracts less than the polymer matrix thus, the interfacial bond strength increases. For Kevlar fibers the transverse contraction of hydrogen bonded molecules is more than the isotropic polymer matrix resin. Thus the interfacial bond strength and adhesion decreases. However, the interfacial adhesion of carbon/epoxy composite shows very tiny sign of temperature dependence (Hartwig 1984).
4.3 Molecular motion and relaxation behavior of matrix resins

The chemistry of polymer matrix resin has a great impact to understand the potential of composite materials. The major polymer matrix used in advanced polymer matrix composite is thermosetting polymer matrix. Although, fiber serves as the load-carrying members, matrix binds the fibers together, and therefore the mechanical properties are decisively dependent by the resin matrix. Curing of amorphous resin leads to cross-linking, chain branching, chain extensions. It impacts high stiffness, high strength, and good thermal and oxidative stability. As the curing proceeds, the glass transition temperature (Tg) of the growing chains increases as the network molecular weight increases. The low temperature curing resins have Tg as high as 120°C. However, 120°C curing glass/epoxy composites have higher ILSS value as well as high flexural strength (Dodiuk et al. 1991). Glass transition temperature (Tg) measured by the Differential scanning calorimeter (DSC) in modulated mode. It covers two time scale of measurement fast one (fixed by the modulation time period) and a slow one (fixed by average, underlying heating or cooling rate) of the polymer matrix resin (Bolleret et al. 1995).

At low temperature several rules are purposed to polymer matrix to achieve its optimum properties. The main advantage is its cross-link density which influences the mechanical properties. Water penetration in composite materials of different interfacial strengths has been studied and explained as the result of two parallel processes, i.e., diffusion through the polymer matrix and through a network of micro-channels formed along the imperfectly bonded polymer-fiber interface. Such channels along the exterior of the loose fiber are presumed to contribute mesoscopic “free volume” to the composite which is conductive to diffusion. An analytical method based on an adaptation of the free volume theory approach is proposed for estimating the
incipient looseness and any further interfacial relaxation caused by water absorption in composite materials.

**Fig 4.11**: Idealized representation of interfacial free volume of annular thickness $h$, around an imperfect bonded fiber radius $r$ in a composite. (Kim and Mai 1998)

Free volume and $T_g$:

Upon a gradual temperature decrease polymers (especially whose with irregular structure or composed of monomers fairly different in their structure and volume) form a glassy state (i.e. undergo the glass transition). The glass transition temperature is a function of molecular architecture, monomer units, presence of impurities or low molecular weight species and the rate of temperature changing. Normally there is some free space between polymer monomers even in melt. In general one can distinguish between the total volume and the occupied volume. The difference between these two considered to be a free volume. The amount of the free volume changes with temperature.
Fig 4.12: Schematic volume-temperature diagram amorphous polymer showing the temperature depends on the free volume (Kim and Mai 1998)

4.3.1 Relaxation behavior and glass transition temperature (Tg)

The shift of molecular chain and group with the unfreezing of molecular mobility upon warming is the cause of appearance of glass transition temperature (Tg). At low and medium temperature, a limited mobility of molecular parts becomes active in taking part of a weak glass transition. Amorphous polymers obey two types of position changes

a) Tunneling  b) Potential barrier jumping

Fig 4.13: The movement of amorphous polymer molecules.
These place change can have drastic effect on the mechanical properties of the polymer matrix which influence the properties of the composite material. The tunneling and potential barrier jumping of molecules associated with time interval which called relaxation time. The mechanical behavior of polymer matrix solely depends upon the relaxation time of matrix. In the absence of force it follows the state of thermal equilibrium position. When force is applied they disturb from their original position with the relaxation time. In contrast to the applied load it also depends upon the temperature. At low temperature the relaxation time is more whereas at very low temperature the relaxation time is shorter because tunneling transition plays the dominant role. At elevated temperature, the potential barrier jumping plays the major role which associated with relaxation time.

4.3.2 Effect of Tg on mechanical action

Tg is used for evaluating the flexibility of a polymer molecule and the type of response the polymeric material would exhibit to mechanical stress. Polymers above their Tg will exhibit delayed elastic response (visco-elasticity), while those above Tg will exhibit dimensions stability. Chain flexibility, intermolecular forces, chain geometry, molecular weight and stiffness of the cross linking chains are important factors for Tg which are not important for free volume (Lu et al.1990). However, change in Tg value directly related to the molecular relaxation processes of the polymer matrix (Jurgen and Schawe 2002; Min et al.1993). General commonsense prevails that higher the Tg better the mechanical properties. Above Tg value
polymer matrix resin trend to thermo-oxidative degradation. Fibers are stable below Tg but the mechanical properties of the interface region can undergo degradation which ultimately affects the durability of the composite material (Barjasteh et al. 2009). The interphase material has a lower glass transition temperature, higher modulus and tensile strength and lower fracture toughness than the bulk matrix. Thermal conditioning is toinduct further polymerization process with the development of penetrating and/or semipenetrating network at the fiber/matrix interface. The response of fiber/matrix interface within the composite plays an important role in determining the gross mechanical performance, because it transmitting the load from the matrix to the fibers, which contribute the greater portion of the composite strength. Better the interfacial bond better will be the ILSS, de-lamination resistance, fatigue and corrosion resistance.

Viscoelasticity (elastomer) behavior at low temperature

At low temperature especially below the glass transition temperature polymer matrix resin shows tiny visco-elastic behaviour. The degree of freedom decreases with decrease in temperature (Ahlborn 1988). Due to the inclement climate of Russia, low-temperature studies of fibrous composite have been vitally important for the successful development of industries and transportation. The matrix resin undergoes lowrate of deformation, low rigidity, large difference between shear modulus and bulk modulus, and significant losses of mechanical energy in dynamic deformation. These unique properties are realized in the temperature range close to room temperature. The low-temperature resistance of polymer is their ability to preserve this set of unique mechanical properties
at a decrease of temperature. The rate of the rubberlike deformation component is hundreds of times lower even at high temperatures, and it sharply drops down at a temperature decrease.

Environmental attack can degrade fiber/matrix interface mostly by mechanochemical principle. Thermal aging behavior of epoxy resins is of special interest because of their expanding use for structural applications where increased temperatures are common environmental conditions. The diffusion coefficient of polymer chain has a strong power-law dependence on the degree of polymerization. Polymers above their Tg will exhibit a delayed elastic response (visco-elasticity), while those above Tg will exhibit dimensions stability. Chain flexibility, intermolecular forces, chain geometry, molecular weight and stiffness of the cross linking chains are important factors for Tg.

4.4 Mechanical properties of FRP composites at low temperature

The mechanical property of composites are the reflection of properties of individual constituents not following the rule of mixture, but the temperature-induced integrity of each phase of the composites are to be critically considered for the evaluation and prediction of property at different temperatures.
Temperature has a great role in changing the deformation behavior of the materials, but the dominance of it differs from material to material. The deformation theory of polymer is highly sensitive to fluctuation of temperature.

### 4.4.1 Deformation characteristic of FRP at different temperatures

The advantages of composites material take the market as an exciting option for wide range of applications. A judicious selection associated with fiber reinforcement, polymer resin matrix, and the interface/interphase offer unique physical and mechanical properties. However, a proper and uniform load transfer across the interface region between fiber and matrix is also big important in composite material. Environment and temperature have the unwilling effect on these valuable properties, leading to premature failure and fracture of the material. These factors have great effect on the life span of the fiber reinforced composites. A number of potential solutions have been proposed to conquer these limitations.
Polymeric composites are susceptible to temperature and moisture when operating in changing environmental conditions. It behaves as ductile manner at room temperature may become brittle at low temperature and show viscoelastic behavior at elevated temperature. Thermal aging behavior of epoxy resin is of unique value due to their expanding use for structural application where increased temperature is common environmental conditions. However, with these swing behavior of material at different temperature alter the mechanical properties which leads to failure. The synergistic effect of thermal and mechanical stresses may cause a change in mode and location of failure as well as a change in threshold load factor needed to cause failure. It is very difficult to generalize the effect of change of temperature. The matrix dominated properties are such as compressive, flexural, shear and transverse properties are most affected by
the temperature dependence on the matrix (Kellogg et al. 2005). Thermal conditioning often imparts better adhesion between fiber/matrix interfaces (Ray 2006). When considering the temperature dependence for the mechanical and physical properties of polymeric materials, various relaxation behaviour are critically important (Lu and Jiang 1990). A dynamic mechanical relaxation occurs in polymer molecule because of heat transfer between the intermolecular mode (strain-sensitive mode) and the intra-molecular mode (strain-insensitive mode) (Yano et al. 1995). Thermal degradation of resin matrix undergoes chemical reaction and physical changes. Chemical reaction as oxidation, cross-linking, while physical change is the visco-elastic behavior of matrix resin (Naruse et al. 2001). The visco-elastic yield nature depends upon the time, temperature and loading rate. At the macromolecular aspect chain scission and cross-linking affect the polymer network and thus, alter the mechanical properties of the oxidized layer. The hindered shrinkage of the oxidized layer induces a stress gradient susceptible to initiate and propagate cracks (Colin et al. 2005). Thermal conditioning behavior of fibrous composites is important, because of their vast use for structural applications, where increased temperatures are common environmental conditions. Fracture processes of polymers are strongly influenced by deformation or yielding processes which depend on temperature, time and loading rate. At very low temperature no yielding is possible in the material and the fracture is brittle. At high temperatures two characteristic phenomena occur after the yield point: strain softening and strain hardening (Naruse et
The specimens tested at a lower temperature are characterized by a greater level of micro-cracking and de-lamination. These effects are believed due to higher thermal residual stresses (Colin et al. 2005). The heterogeneous and anisotropic nature of the fiber and matrix results in different in thermal expansion and contraction mismatch which generates thermal stresses.

**High Temperature**

When subjected to elevated and high temperatures, the mechanical properties of FRP composites, such as the E-modulus and viscosity, experience significant changes. At a certain temperature, a composite material can be considered a mixture of materials that are in a glassy, leathery, rubbery or decomposed state (Ray 2004). The mechanical properties of the mixture are determined by the content and the property of each state. Thermal conditioning at above ambient temperature might possibly improve adhesion level at the interfaces. The interphase is defined as a region which is manifested as a result of bonding and reactions between the fiber and the matrix. This region is the site of synergy in composite materials and its influence to overall mechanical properties is significant (Ray 2006). It is generally recognized that the bond strength variation at the interface greatly affects the integrity of composite materials. The bond strength depends on quality of interfacial adhesion. Adhesion chemistry at the interface may be influenced by post-curing phenomena and this effect is supposed to increase with more conditioning time limited by some optimum value (Mader et al. 2004). Thermal
conditioning causes matrix shrinkage due to loss of volatile material and additional cure of matrix resin (Wang et al. 2007). The fracture behavior of the CFRP composites at different temperature is complicated. Various fracture modes as fiber breakage, fiber/matrix interfacial fracture, and de-lamination occurred between adjacent plies of the laminates. Inter-laminar shear strengths value decreases nearly linear by increasing temperature of the material (Aktas et al. 2009). Whereas GFRP composite losses their rigidity and strength at room temperature and high temperatures (Morioka et al. 2001). Above the glass transition temperature ($T_g$), polymer composites are prone to thermo-oxidative degradation. Although the fibers are stable below $T_g$ but the matrix and especially the fiber–matrix interface can undergo degradation that affects the physical and mechanical properties of the composite structures over time. Thermal conditioning is to induce further polymerization process with the development of penetrating and/or semipenetrating network at the fiber/matrix interface. The response of fiber/matrix interface within the composite plays an important role in determining the gross mechanical performance, because it transmitting the load from the matrix to the fibers, which contribute the greater portion of the composite strength (Barjastehet al. 2009).

Low Temperature

The polymer composite have vast application at cryogenic temperature as space, superconducting magnet and electronic technologies (Reed et al 1997). Potholing or
localized surface degradation, de-lamination, and microcracking are some of the more dramatic phenomena that can occur as a result of cryogenic cycling (Salin et al. 1996). Compressive residual stresses developed due to differential thermal contraction, influence the overall thermo-mechanical properties of the composite. In some cases, the resulting stresses are sufficient to initiate plastic deformation within the matrix immediately around the fiber (Borje et al. 2000). The thermal residual stresses can also be large enough to initiate material damage such as matrix micro-cracking. Potholing / localized surface degradation, delamination and microcracking are some of the more dramatic phenomena that can occur as a result of cryogenic cycling. These micro cracks can reduce both the stiffness and the strength of the material, as well as act as sites for environmental degradation and nucleation of macro cracks (Timmerman et al. 2002). The propensity for micro-cracking and the micro-crack morphology depends on the type of fiber and matrix used. At low temperature the cross-linked polymers shows brittle behavior and it don’t allow relaxation of the thermal residual stresses.

**Low temperature behavior of epoxy**

The mechanical and thermal properties of several types of epoxy systems were designed based on the chemical structure, network structure and morphology aiming at cryogenic application. Epoxy resins have been widely used as the matrix of composites material due to their good electric insulating, mechanical, and easy fabricating properties (Ueki et al. 2005). Additionally the epoxy-based composites have also been used for cryogeniccap-
applications. At low temperature the internal stress due to the thermal contraction is generated in a matrix resin. Fracture of the matrix is induced when the thermal stress induced stress intensity factor exceeds the fracture toughness of the resin (Hartwig 1994). It is, therefore, indeed the fracture toughness of the epoxy resin is improved even at cryogenic temperature. To attain the high performances of polymers, it is necessary to control the molecular structure, e.g. chemical and network structure. To control the morphology of the polymers is also needed when the different types of polymers are blended. To improve the fracture toughness of epoxy the plasticizer is usually added. The morphology such as the sea-island structure and interpenetrating network also determine the physical properties of epoxy (Sawa et al. 1995). When the morphology is optimized, the modified toughened polymer could be obtained showing high crack-resistance without degradation of other properties. Changing the types and amount of modifier or the curing process can change the morphology. It is very important to clarify how to control the molecular structure to obtain high performance polymer effectively and economically at cryogenic temperatures (Kanchanomai et al. 2005).

4.4.2 Implication of hygrothermal environments on failures

As with any engineering material, whilst in service, composites can be exposed to a diverse range of environments and degrading factors, the severity of which depend upon the particular application. Glass-fiber reinforced (GRP) composites are often used in
marine craft such as canoes, fishing trawlers, patrol boats and naval mine hunting ships and in the non-pressure hull casing, sonar dome and masts of submarines (Wilde et al. 1993). The use of fiber-reinforced composites (FRPs) in aircraft structures is increasing as new generations of aircraft take advantage of their attractive structural properties. Weight change behavior of FRP composites in humid and thermal environments appears to be complex phenomena. In particular, the fiber/matrix interface is highly prone to in-service degradation (Ray 2006).

Several models have been put forward to address the issue of the state of water molecules in epoxies. Zhou suggested that there are 2 types of water molecules with single/double H bonds to epoxy networks, respectively, while Marechal supposed that water molecules either establish 2 hydrogen bonds/donot establish any H bond with their H atoms. But Liang Li et al. investigated that 2 kinds of water molecules existing, in one could be confined into relatively free water, while other could be attributed to bound water forming a strong H bond with hydrophilic groups of epoxy networks. Maxwell and Pethrick studied that the water could exist in clusters in which it was relatively free/could be molecularly dispersed within the resin and bound to it, probably by H bonding (Liang et al. 2005). The absorption and diffusion of water in polymeric material such as epoxy systems is related to the free volume and the polymer-water affinity (Eidelmanet al. 2004). Epoxy based composite laminates absorbs moisture from
the surrounding environment very quickly and attains equilibrium. The equilibrium water content depends not only on the free volume in the matrix (related to relatively free water) but also on how many H bonds are formed between water and network polar groups (Xiao and Shanahan 1997). With PALS and calculations, Yee et al found that equilibrium water content is controlled by free volume fraction at absolute zero (0K), which is decided by the amount of epoxy group before curing (Zheng and Morgan 1993). In other word, the polar groups at the inner surface of free volume provide the bonding sites for water molecules, while the limited space of nanopores restricts the formation of free water-water H bonding [Tsenlglou et al. 2006]. Therefore, water diffuses into the composite material driven by the water gradient. Whitney and Browning reported preferential paths of diffusion due to non-uniform swelling of the resin through the thickness before equilibrium is reached. Thus it appears that before the resin becomes saturated with moisture and a moisture gradient exists in the composites (Wu and Siesler 2003). The effect of moisture on the matrix includes reversible processes, such as hygroelasticity and swelling. The constituent that is most sensitivity to moisture is the fiber/matrix interface, and therefore, moisture promotes damage mechanisms that are controlled by the interfacial performance (Lin and Chen 2005). Moisture wicking along the fiber-matrix interface degrades the fiber-matrix bond resulting in loss of microstructural integrity. The net effect of moisture absorption is the
deterioration of matrix-dominated properties such as compressive strength, interlaminar shear strength, fatigue resistance and impact tolerance (Wagner et al. 1994).

The properties of the fiber/matrix interphase in glass-fiber reinforced composites can play a dominant role in governing overall composite performance. Understanding the interactions occurring at the interphase and being able to tailor them to give a desired composite property are of great importance (Chateaueminois et al. 1994). The sizing surface free energy and its solubility in the matrix were shown to strongly affect interphase formation, fiber-matrix adhesion and composite shear and flexural strength (Feih et al. 2005).

In an outdoor environment aircraft are subject to continuously varying temperature and relatively humidity and as a result there will be periods of exposure that will produce moisture absorption and moisture desorption in an FRP laminates (Morozova et al. 2004). In diffusion theory, the rate of absorption was mainly a function of temperature and the amount of moisture absorbed was a function of the relative humidity (Abdelkader and White 2005). However, epoxy resins will absorb moisture from their surroundings (up to 3-4% of their original weight) which causes a lowering of the Tg; 1% absorbed water reduces the Tg by 20ºC (Sanjee et al. 2005).

For a given brittle-fibre/brittle-matrix composite, high strength requires a strong interfacial bond, but this may lead to low fracture energy absorption. However, by
proper control of the physical and mechanical properties of the fibre--matrix interface
high strength characteristics can be combined with high toughness. In order to fully
utilize the potential of such composites without introducing a reduction in strength, it is
necessary to understand the failure mechanisms leading to eventual fracture. Failure of
fiber-reinforced plastic laminates is a slow and lengthy process. Transverse cracks are
initiated at low loading levels in the first vulnerable plies and continue to accumulate
under increased loading conditions up to saturation crack density.
Durability of glass-fiber/polymer composites is dictated by the durability of the
components: glass fiber, matrix, and the interface. Environmental attack by moisture,
can degrade the strength of the glass fiber; plasticize, swell, or microcrack the resin; and
degrade the fiber/matrix interface by either chemical or mechanical attack.

4.4.3 Loading rate sensitivity of FRP at low temperature

Mechanical behavior

In addition to strength and modulus another important property of a composite is its
resistance to fracture. A measure of fracture resistance of a material is given by the
specific work of fracture, or fracture toughness, and is defined here as the energy
required for creating unit area of new transverse fracture surface of the composite. When
a composite is loaded there is widespread microscopic damage arises throughout the
body. Large damage can be sustained to a critical value at which failure occurs by the
propagation of cracks. These cracks are much more complex in nature than cracks inhomogeneous materials. The failure of a composite involves the fractures of the load-bearing fibers and the matrix as well as a complex combination of cracks propagated along the interfaces. Therefore, fracture toughness of a composite depends not only on the properties of the constituents but significantly on the efficiency of bonding across the interface. To understand the properties of the interface and its role in controlling fracture, it is essential to know the mechanisms of adhesion at the interface involved. Since the nature of bonding is dependent on the atomic arrangement and chemical properties of the fibre as well as on the molecular conformation of the matrix, it follows that the interface is specific to each fibre-matrix system. The major mechanisms according to Hull 2 include adsorption and wetting, interdiffusion, electrostatic attraction, chemical bonding and mechanical bonding. In addition, hydrogen bonding, van der Waals forces and other low energy bonds may also be involved.

4.4.4 Status of interfaces on mechanical behavior

Fiber-matrix interface is highly inclined to in-service degradation of FRP composite. The physico-chemical and mechanical aspect of the interface is an important area for the composite material. The theories of adhesion and type of bonding play a great role to obtain the optimum properties of interface region. Furthermore, the macroscopic, microscopic and nanoscopic nature of interface characterization is required for great useful of the advanced polymer composite.
Theory of adhesion between the fiber and the matrix followed by various mechanisms, also have some impact on absorption, wetting and electrostatic attraction at the interface region. The nature of bonding which is crucial for the adhesion is not only depending upon the molecular arrangement, but also the morphological and diffusivity properties of the fiber and the matrix.

The strength of interface region may be due to formation of interdiffusion bond between the fiber and matrix. The bond strength in polymer matrix composites will depend on the amount of molecular entanglement, the number of molecules involved and the strength of the bonding between the molecules (Kim and Mai 1998). Interpenetrating network (IPN) and the interdiffusion are the two examples for the explanation of the adhesion between fiber and the polymer resin matrix.

We assume that interphase region is in 3-D form and act as a softer phase than the bulk matrix. The average modulus of the interphase of a thickness 500nm formed between a single carbon fiber and epoxy matrix is about one-quarter of that in the bulk matrix. However, the presence of stiff fiber mitigates the effect of a soft bulk matrix in close vicinity of the fiber (Garton et al. 1985).

4.4.5 Failure revelations through microscope and microanalysis

Fractography analysis of a failed polymer composite material is now a challenging experience. PMC material shows number of failure modes which are the root cause of
degradation of a component. The failure may be due to environment or may be in-service degradation. Thus there is a need of failure analysis through microscope and microanalysis.

Currently available most powerful tools for the characterization of failure component are: Fourier transforms infrared spectroscopy (FTIR), Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Auger electron microscopy (AES). Each technique has some complexity, advantages and limitations. This section covers some microscopic techniques which are useful for the fractography analysis.

**Spectroscopic analysis**

**FTIR –Imaging:**

FTIR spectroscopy has been extensively used for surface characterization of polymer matrix surface, indication of various functional groups of the surface of the material and the chemical modification at the interface region. In case of GFRP the reactivity of the silane coupling agent with the epoxy resin was found to vary with drying conditions of the silane coupling agent. Infrared spectroscopy gives information on molecular vibrations or more precisely on transition between irrational and rotational energy levels in molecules. When
infrared light of that frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased. An infrared spectrum is obtained when the frequency of molecular vibration correspond to the infrared radiation absorbed. The normal range of an infrared spectrum, used by organic chemist for structural work, extends from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\).

FTIR Images were sequentially acquired during the curing time in the region of view, which included the glass fiber/epoxy mixture interface.

![FTIR Image](image)

**Fig 4.15:** Evolution of the FTIR spectra for the epoxy–amine mixture as a function of the curing process. (Benito et al. 2003) Copyright permission 2003 Elsevier.

The mechanism of the curing can follow two different but simultaneous paths. The curing process of an epoxy system at the interface formed with a silane coated glass fiber was studied by using FTIR imaging. Chemically specific images for OH and H-N-H within the system were obtained. The analysis of these images suggests that there is a variation in the chemical structure of the
matrix from fiber to polymer bulk due to different conversions arising from a gradient in the initial composition (Benito 2003). It was observed that the rate of curing reaction changed depending on the distance to the glass fiber and this change was also associated to changes in the stochiometry. There are certain limitations of refraction and reflection at the fibre surface in the spectroscopy that will finally affect the FTIR spectra of glass/epoxy composites. Due to this only a small percent of light reaches the detector. It is difficult to separate these optical effects from the samples. However these optical effects can be minimized by taking FTIR spectra over the same region of the micro-composites.

**Atomic force microscope (AFM)**

This is the most advanced tool for the characterization of the composite material in nanometer scales. Application of AFM growing rapidly as it is useful for observing surface topography of the composite material. This technique can be applied both conductive and non-conductive specimens. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, and magnetic forces. As well as force, additional quantities may simultaneously be measured through the use of specialized types of probe. CFRP composite
showing height image scan in tapping mode after hygrothermal treatment at different time interval.

**Fig 4.16:** AFM topography images of the same cross-section area of AS4/VRM34 using TappingMode (a) and contact mode (b). The scan size was 30 · 30 lm. (Wang Y. et al 2007) Copyright permission 2007 Elsevier.

Thermal degradation of plastics involves chemical reaction and physical changes. Chemical reaction is represented by oxidation, crosslinking and further reaction of unreacted monomers, while physical change is typical of viscoelastic behavior (Narese et al. 2001).
Temperature Modulated Differential Scanning Calorimetry (TMDSC)

In temperature modulated DSC (TMDSC) the rate of heating are varied by overlapping the underlying linear heating rates with a sinusoidal temperature modulation. In application aspect it separate the reversible nature of thermal expansion from irreversible deformation which arising from creep under the applied load or changes in dimensions due to relaxation of orientation. It helps for generating image based on local changes thermal expansion of a specimen (Price DM, 2001). The DSC measurements were performed on a Mettler-Toledo 821 with intra-cooler, using the STAR software with Temperature 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 $10 \text{ C min}^{-1}$ 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. If, however, amodulated temperature program (such as those used in modulated temperature differentials scanning calorimetry (MT-DSC)) is employed (rather than the
conventional linear temperature ramp), then it is possible to separate the temperature dependent thermal expansion from the time (and temperature) dependent creep or stress relaxation behaviour.

![Graph of Tg variation](image)

**Fig 4.17**: Schematic representation of hygrothermal treatment of glass and carbon epoxy micro-composites respectively showing Tg variation.

It appears that the change of the glass transition temperature as a function of the conversion is directly related to the molecular relaxation processes (Jurgen et al. 2002). During the isothermal cure of an epoxy resin the system changes from
a viscous liquid to a highly crosslinked network. The enthalpy and the volume of the system are expected to decrease continuously during the curing until the vitrification process.

Fibrous composites are increasingly being used in many applications owing to various desirable properties including high specific strength, high specific stiffness and controlled anisotropy. But unfortunately, polymeric composites are susceptible to heat and moisture when operating in changing environmental conditions. The structural integrity and lifetime performance of fibrous polymeric composites are strongly dependent on the stability of the fiber/polymer interfacial region. Plasticization induces plastic deformation in addition to lowering the Tg, whereas swelling is related to the differential strain which is created by the expansion force exerted by the liquid while stretching polymeric chains. It is generally believed that the polymer is likely to be tough if homogeneous yielding occurs. Even brittle crack propagation in polymers usually involves localized viscoelastic and plastic energy-dissipating processes taking place in the vicinity of the crack tip. The propagation of the debonding cracks may involve breaking of the primary and secondary bonds between the fibre and the polymer matrix. It should be noted that multiple matrix cracking may represent a significant source of toughness.
Glass transition temperature of matrix resin is an utmost important parameter to design and develop polymeric composites. The reliability and durability of FRPs are critically dependent on it. Moisture and temperature are few worst environmental factors adversely affecting the structural integrity and mechanical performance of FRPs. Moisture ingress and changing humidity along with change of temperature quite possibly and eventually change the $T_g$ of a polymer matrix. The change of this temperature has to be measured with most accuracy and reproducibility by means of advanced thermal analyzer like Alternating DSC. The change of chemistry at the interphase by the implication of moisture ingress needs to be further assessed by FTIR-Microscope by selected area imaging. The stress transfer efficiency and consistency is decisively controlled by the physical and chemical nature of the interphase area. An approach may be suggested here to evaluate the status and strength of the phase by AFM technique. The more precise and critical analysis of the environmental-induced health of the interphase is to be predicted and concluded, the more potential and promises of the FRPs are to be realized and explored.

4.5 Possible failure modes of FRP composite at low temperatures (Energy-absorbing mechanisms): Micromechanics and progressive failure
Fibrous composites are now have monstrous application including aircraft, space shuttle, motor vehicles, sporting goods, and wide range of military equipment. They are extremely broad and versatile material. While we migrate from metal world to the FRP world, structural designer still face challenges when it comes to mechanical properties of FRP composites at various environmental factors. Advanced polymer composites consists of polymer matrix reinforced with high strength and high stiffness fibers. The effect of environment can dramatically change the instantaneous response of the composite. In general to achieve optimum performance, composite designers strive for volume fraction for 60 %, but generally $V_f < 55\%$. With 60 vol% fiber content unidirectional CFRP shows transverse failure strain at only 0.7-0.9% which is lower than the 5-6% strain of the pure anhydride cured DGEBA epoxy resin (Hughes 1991). The classic definition of the interface in the fiber composites is a boundary formed by reinforcing fiber and matrix, which is critical to the overall composite portrayal. Too weak an interface gives low composite strength and stiffness; too strong and the composite will be brittle (Greenhalgh 2009). In addition, fracture surfaces and fracture paths are found to vary with the nature of fiber-matrix interface and its dependence on the environment and temperature. Understanding composite failure underpins development of failure criteria. Factors such as temperature, moisture and loading rate, can have a considerable effects on the fractography behavior. Fracture analysis is complicated for polymers since, besides of temperature, and time
dependence, there are involved effects from plastification, chain orientation and adiabatic temperature rise (Hartwig 2004).

A judicial control of mechanical behavior of interface region leads to high toughness value of composite material. Brittle fiber/brittle matrix requires strong interfacial adhesion, which leads to low fracture energy absorption (Jang and Kim 1991). Due to thermal contraction a tighter packing and thus a higher bond strength at decreasing temperature results. At very low temperature, chain or chain atoms have nearly no thermal energy capable of counteracting the binding potentials. Induced fracture processes are crazing, necking, or plastification. In homogeneous stress distributions lead to stress contraction which reduces fracture strength.

A high temperature, matrix-dominated properties of CFRP will be influenced by the softening of the matrix as the temperature approach the matrix glass transition temperature value. However, at low temperature, polymer matrices are become brittle. Fiber dominated properties will generally be unaffected and the mechanical properties as well.

4.5.1 Matrix deformation and cracking
Thermosetting polymer matrices are amorphous in nature. They follow the state of non-equilibrium which is the responsible for sensitivity of various environmental factors as temperature, humidity, moisture as well as experimental parameter and loading rate. Application of different loading rate may interact with above such parameters and accelerates the failure and fracture of polymer matrix composite. Various failure modes are seems too occurred while degradation of composite material formed. The role of matrix in PMC is of 3 major importances, i.e., it is used to protect fibers against environmental attack; it serves as a load-transferring medium, and it also act as an energy-dissipation outlet of arresting crack propagation. The matrix materials in FRP are extensive and varied in properties. Theses thermosetting resins converted from low molecular weight (polyfunctional monomers or oligomers) with low viscosity to three-dimensional cross linked networks which are rigid in nature and quite brittle. The matrix materials usually have relatively low modulus, and strength values and comparable or higher ductility values (Jang 1994). Epoxy resins generally used high performance fiber composites. In liquid state they can be used as impregnation material for wet-layup technique. The mechanical properties of
composites at low temperatures are influenced by the matrix. At low temperature thermal prestress is crucial. This reduces effective strain to failure and is the source of microcracks in the matrix (Hartwig 2004).

**Table 4.7.** Fracture strain of matrix at 4.2 K and fibers are complied below (Hartwig 2004)

<table>
<thead>
<tr>
<th>Matrix and fibers</th>
<th>Fracture strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>2%</td>
</tr>
<tr>
<td>Fiber glass</td>
<td>3%</td>
</tr>
<tr>
<td>Carbon fibers</td>
<td>1.2-2.2%</td>
</tr>
<tr>
<td>Kevlar fibers</td>
<td>1.5-2%</td>
</tr>
<tr>
<td>Thermoplastic matrices</td>
<td>3-4%</td>
</tr>
</tbody>
</table>

The fracture morphologies associated with matrix-dominated fracture are described. The approach is to present the morphologies associated with epoxy based polymer matrix composites with glass, carbon, Kevlar fiber reinforcement.

Matrix microcracking is the source of damage in laminates which are intralaminar or ply cracks that transverse the thickness of the ply
and run parallel to the fibers in that ply. The initiation of micro-cracking is depend upon strain which means microcracking increases as the thickness of the 90 plies decreases the first-ply failure theory predicts that the strain to initiate microcracking will be independent of ply thickness. Microcracks in carbon fiber/epoxy laminates always formed instantaneously across the entire cross sectional area of the 90° plies.

The first form of microcracks causes very mild effects in the thermo mechanical behavior of composites. With increasing the applied load and loading speed, additional microcracks are generated and they are the incentive for failure of polymer matrix composites. We can assume that, microcrack density as a function of loading condition and applied load. After the initial microcrack density typically increases very rapidly with applied load. At high crack density, microcrack approaches to its saturation damage state. Most microcracking experiments have been conducted on laminates under uniform stress state such that the stress state in the 90 plies is uniform prior to micro-cracking.
Fig 4.18 Matrix cracking (a) and multiple matrixes cracking (macro cracking) (b)

As we discussed at low temperature the matrix behaves in brittle material, morphology such as riverline marking and texture microflow can be observed in the resin. These failure marks shows the sign of local crack growth directions. These marks are less apparent when the toughness of the matrix increases.

Below figure show a visible riverline marking with scraps, potholes and textured microflow. Somehow we considered the riverline mark-
nings as most valuable features for diagnosing crack growth directions. Besides that, other important matrix fracture is scraps and ribbons. When multiple microcracks are formed and begin to propagate in several planes, and they subsequently converge onto one plane. When two crack planes converged, the boundary between these planes shows a sharp step can form. This is an example of formation of scarps. The global growth direction in this figure is shown as (top to bottom). It should be noted that the local crack growth inferred from the textured microflow is from the fibers into the surrounding resin. These are indications of the absorption of energy by local deformation. Fig (4.19) shows four converging crack planes in a resin rich region within a glass/epoxy polymer composite at low temperature treatment. A further feature, a ribbon like structure also formed at low temperature treatment. These are developing if the crack planes overlap before they coalesce to form scarp (Greenhalgh 2009).
Fig 4.19: Cryogenically treated GFRP composites showing resin rich region with riverline marking © And cryogenically treated GFRP composites showing ribbon like structure (d)

Considering the influence of low temperature on the fracture micro-mechanisms in composites; the matrix is brittle and residual tensile stresses in the matrix are promoted. At very low temperature resin embrittlement dominates phenomena and thus composite toughness decreases. As the temperature increases very close to the glass transition temperature of the matrix, it becomes ductile and behaves as softer material. As shown in figure below, at high temperature fiber
imprints are formed with stresses generated at the edge point. Matrix behaves as softer means the process zone is spread over a large depth, degree of bridging leads to increase (Greenhalgh 2009).

Fig 4.20: Thermal conditioned GFRP composite showing fiber imprints region (a) and stresses generated at the edge of the fiber (b).

Above discussions associated with matrix failure modes at high as well as low temperature, which are responsible for integrity and du-
rability of polymer matrix composites. However, the generic fracture morphologies such as matrix cleavage and matrix failure in prepreg GFRP composites. It accepted that voids and porosity have prejudicial effects on the composite performance. There are many factors which are responsible for these voids formation. This is primarily due to trapped of volatiles materials including air, inclusions. These volatiles materials are either entrapped during the fabrication or the water or residual solvents from the prepregging process Fig (4.21). When the matrix behaves as brittle, the energy of fracture is fairly low and there is little step marking formed during failure, which is refereed to cleavage marking. The characteristic feature of cleavage fracture is flat facets which generally are about the increasing size of 9.22μm to 20.6μm.
Identification of the cause of fracture through fractography has become a standard investigation tool.

4.5.2 *Inter fiber fracture (IFF) and fiber pull-out*
Fibers are of different forms natural, regenerate and synthetic. The polymer composite consists of fibers embedded to a matrix with prominent interface (2D) or interphase (3D) region. The fibers are act as load-bearing members with high strength and modulus. Due to this it has enormous novel applications. Simultaneously, research in this area is very active in state. The most commonly used fibers are glass fiber, carbon fibers, and Kevlar fibers. A key feature of this interface bonding is due to formation of strong ionic and covalent bond. As the fibers are brittle in nature, there mechanical properties are controlled by the study of fracture behavior. Thus, there is a deeper grasp of this failure mechanism of fiber fracture is indeed. The reinforcement fibers may be continuous or filaments or chopped fibers or whiskers. Advanced PMC are being used in many sectors as automobile, industries, and aerospace structures. A superior combination of high strength, stiffness and density makes the carbon fiber eligible for these advanced applications. Whereas research on glass fiber seen an explosive growth due to its application in the area required of high tensile strength. In general, highly oriented fibers such as aramid fail in a fibrillar fashion. The term fibrillar fracture here signifies that the fracture surface is not transverse to the axis but runs
along a number of planes of weakness parallel to the fiber axis. Considering above some failure modes of fiber-dominated morphologies is discussed.

Fig 4.22 GFRP composite showing uniform failure of fiber (a)
And GFRP composite showing fiber pull-out and brittle failure (b)

Glass/epoxy reinforced composites the bond strength is reported to be around 33 MPa E-glass/epoxy and with silane treatment it is 49 MPa. The fiber/matrix interface is usually quite poor and shows brit-
tle failure at the end. Whereas carbon/epoxy polymer composite the bond strength is 57 MPa, the same for Kevlar/epoxy polymer composite is about 38 MPa. In this Figure 4.22(a) we can assume, the fibers tend to fail homogenized with proper interfacial bonding. Whereas in Fig 4.22 (b) the fibers are tend to fracture independently at different points along their lengths. Fracture surfaces are seemed to be flat. Carbon fiber and glass fibers are inevitably brittle material, so radial patterns appear at the fiber breaking end. Aramid family fiber (Kevlar) exhibits different failure modes due to non brittleness. Brittle fibers have low fracture strain and low energy absorbing capability (Jang 1994). Flexure response of PMC is a complex phenomenon. The material behaviors and the loading condition may able to influence the behavior of energy-absorbing mechanism in composites.

Fiber pull-out appears when the fibers are embedded in a tough matrix. Fibers can fracture early at the weak cross section point, which is not necessarily the direction of crack propagation. As the applied loading rate increases the fracture proceeds, the broken fibers will likely pullout from the matrix. This is the reason for the mechanism of fiber pull-out in PMC composite.
Fig 4.23: Hygrothermal treated GFRP composite showing fiber pull-out (a) and GFRP showing strong adhesion between the interphase region (b).

Presented in Figure (4.23 a) fiber pullout and fiber fracture end of hygrothermally treated GFRP composite for 10 hr. In Fig (4.23 b) a strong adhesive failure are expected to occurred. This failure confirmed by the cohesive failure produced by the GFRP composite. The weak boundary layer (WBL) is the region of low cohesive
strength between fiber and matrix region. WBL provide a weak interface bonding, promoting interface debonding and fiber pull-out as shown in above figure (Brewis 1993).

Such a crack which runs parallel to the fibers through the entire thickness of a layer is called Inter Fiber Fracture (IFF). The term IFF comprises both cohesive matrix fracture and adhesive fracture of the fiber/matrix-interface. The crack itself does not grow slowly but is generated spontaneously and stopped only by the fibers of the neighboring layers of different fiber direction. Typically, at the tip of the IFF crack small delaminated zones can be observed. The cohesion between the broken and the neighboring layers is affected locally but the integrity of the laminate is still preserved. It does not fall into parts as it would naturally be the case if the laminate consisted of layers with only one fiber direction.
Fibers stand among the stiffest and strongest materials either present in nature or manufactured by man. They are used in structural components, embedded in a matrix which maintains the fibers oriented in the optimum direction, distributes the concentrated loads, protects the fibers against wear and chemical attack from the environment, and provides the transverse stiffness to avoid buckling in compression. Fracture of fibers (4.24) during processing or in service is generally an undesirable feature. In polymeric fibers, the fundamental processes leading to failure are chain scission and/or chain sliding or a combination thereof. Service environment can be a major determining factor in the failure process of fibers. Fracture in fibers, as in bulk materials, initiates at some flaw(s), internal or on the surface. In general, because of the high surface to volume ratio of fibers, the incidence of a surface flaw leading to fracture is greater in fibers than in bulk materials. Fractography, the study of the fracture surface, of fibers can be a useful technique for obtaining fracture parameters and for identifying the sources of failure. In general, the mean strength of a fiber decreases as its length of diameter increases.
Rigid-rod polymeric fibers such as aramid fibers show very high strength under axial tension. The failure in tension brings into play the covalent bonding along the axis, which ultimately leads to chain scission and/or chain sliding or a combination thereof. However, they have poor properties under axial compression, torsion, and in the transverse direction.

As the orientation of chains in a fiber becomes more parallel to its axis, its axial tensile modules \( (E) \) increases but the shear modulus \( (G) \) decreases, i.e. the ratio \( E/G \) increases rapidly. During failure involving compressive stresses, fibrillation occurs, which results in a large degree of new surface area. This fibrillation process results in high-energy absorption during the process of failure, which makes these fibers useful for resistance against ballistic penetration (Jang 1994).

Two types of compressive failure modes are important for failure and fracture of polymer composites (Fig 4.25). 1) Microbuckling or fiber orientation of polymeric chains and 2) kink band formation. Former one includes closely spaced chain in a small region of fiber.
And this microbuckling may be the reason for formation of kink band failure mode under compressive loading.

Environmental factors such as humidity, temperature, ultraviolet radiation, and micro-organisms can affect the strength and the fracture process in polymeric fibers. Various failure modes play dominant role (4.26) for affecting the mechanical behavior and durability of the polymer composite material.
Fig 4.26: Above micrographs of glass/epoxy micro-composite with hygrothermal treatment divulge fiber/matrix debonding, fiber fracture, resin rich region, brittle failure of fibers.

4.5.4 Delamination

Delamination is a critical failure mode in polymer matrix composites. Interfacial debonding (delamination) may cause of premature buckling of the laminate. It occurs due to excessive moisture absorp-
tion, loss of fatigue life, decrease in stiffness of the composite. In many practical purposes this problem can be overcome by Finite element methods (FEM) (Swart et al 2000). Research on this failure mode is very extensive and growing rapidly. In short-term treatment of the specimen, damage growth and premature failure occurs due to delamination. However, for long-term, this is lead to load-bearing layers for different environmental factors (Greenhalgh 2009). Delamination of a laminate occurred when the transverse shear force resultant exceeded a threshold value (Jang et al. 1994). Low interfacial shear strength may be the reason of initiation and propagation of delamination. It was reported fatigue delamination growth rate at 77K and at 4K was lower than that of room temperature. The delamination rate at 4K was higher than the 77K temperature (Miura et al 2009).

The delamination is the life-limiting failure process in a composite material. It induces great stiffness loss, local stress concentration and buckling failure of polymer composites. This failure mode arises due to interlaminar stresses from impact or shear loading, foreign particles, or some discontinuities in the structure.
The difference in coefficient of thermal expansion (CTE) between the fiber and the matrix may be the cause of residual thermal stress developed in the material when worked at various temperatures. However, moisture absorption and desorption also the reason behind the formation of residual stress. This would modify the local stress threshold required for interfacial debonding, a potential precursor to delamination nucleation.

Causes of delamination include the high inter-laminar stresses at the free edge, impacts and fabrication defects; low velocity impact of foreign objects is considered one of the most important causes of delamination. Delamination appears at several interfaces increasing through the thickness away from the point of impact and significantly reducing the compressive strength.
Fig 4.27: Scanning micrograph shows delamination of fiber reinforced composite

Blister problem is an example of delamination under load (local stress concentration) under compressive loading the initial void area can spread rapidly which tends to buckling. The required strain energy to separate the bonded layer is the nucleation of delamination
(Senussi et al. 1995). The boundary between two plies of different orientation is the region of delamination where shear deformation formed. This occurs preferentially along the axis of the fiber, since it is the source of least resistance (Purslow 1981). However, at low temperature under mode II loading hackle pattern on the fracture surface is highlighted and delamination occurs due to fiber/matrix debonding (Yasuhide et al. 2011).

4.5. 5 Interfacial damage and debonding
The polymer composite assumed to have excellent bond strength between fiber and matrix. When it is treated in low temperature the original bond strength of matrix is very little importance since it is increased by shrinkage of the matrix onto the fiber surface. The fibers carbon and Kevlar have high transverse thermal expansion due to which they have very less shrinkage effect (Hartwig 2004).

The energy imposed to a composite can be absorbed followed by two mechanisms: elastic and plastic deformation of the material. Plastic deformation mechanisms as shear yielding can be promoted by various techniques to toughen the epoxy matrix. The energy absorbing capability or toughness of a material can be enhanced by in-
creasing either the total area of new surfaces created or the material
deformation capability. We can assume that various failure modes
are formed due to small defects, inclusions. During the crack propa-
gation large transverse tensile stress and interfacial shear stress can
cause fiber-matrix interfacial debonding, delamination and interfa-
cial cracking slightly ahead of the crack tip. Near the crack tip re-
gion a matrix plastic deformation zone occurred. Immediately be-
hind the crack tip the broken fibers can pull out of the matrix. Weak
interface strength can promote extensive debonding, leading to an
increase in impact energy.
Fig 4.28: Scanning micrograph showing toughened matrix with matrix roller (a), matrix/fiber failure (b), a line of weak adhesion level (C) and toughened matrix (d).

On a macroscopic point of view, poor fiber/matrix bond strength is associated with brush-like failure. This means that lack of matrix on the fiber surface. The factors such as, excessive exposure to moisture, temperature, humidity can contribute for the weak fiber-matrix interface strength. In this state load-transfer between the fiber and matrix is reduced. At high temperature, fiber-matrix debonding and matrix ductility plays the dominant role and the residual stress effects are negligible.
If the fiber-matrix interface strength is high, the degree of fiber debonding will be limited before the fiber failure occurs and crack propagates across the fibers. This will lead to a flat, relatively smooth surface, often referred to as brittle failure. If the interface strength is weak, the degree of fiber debonding will be extensive before fiber failure occurs. This leads to broomlike failure.

Delamination and microcracking are some of the most frequently observed damage phenomena that may develop in polymer composites exposed to cryogenic temperatures. The mechanical performance of fiber-reinforced composites is strongly dependent upon the quality of fiber/matrix adhesion. Cryogenic hardening may modify
the local threshold required for breaking of adhesion bondage at the fiber/matrix interface. Most polymers lose their ductile properties below their glass transition temperature. Cooperative chain motions involving main chain bond rotation become extremely restricted.

4.6 Some issues in the interface, matrix and fibers of FRP composites at low temperature

4.6.1 Experimental explorations

Composite materials are tailored from fiber reinforcement and resin matrix which significantly different in physical and chemical properties. They have distinct macroscopic or microscopic scale of the structure. The high strength and stiffness fibers are dispersing in a matrix material, as a trimmer and transfer the load across the interphase region. Interphases in composites are regions that form in the vicinity of the fiber surface and possess distinct properties compared to those of the bulk resin (Jang 1994). One mechanism of interphase formation based on thermodynamic considerations predicts that small monomers preferentially segregate to the fiber surface
(Anashkin et al 1999). Previous investigations have shown that the interphase has a significant effect on composite properties such as strength, toughness, ballistic resistance, and durability. Modification of the interphase could lead to improvements and balance of properties required for a given application; therefore, significant efforts are directed at developing a fundamental understanding of the role of the interphase.

These are the modern engineering materials that have wide applications in a range of areas from aerospace, automobiles and boats to cryogenic equipments such as cryogenic fuel tanks, cryogenic fuel delivery lines, cryogenic wind tunnels and parts of the cryogenic side of turbo-pumps because of their ease of handling, low fabrication cost and excellent mechanical properties (Anashkin et al 1999). When the temperature is decreased down to cryogenic temperature internal stresses are generated in the epoxy matrix due to thermal contraction. Fracture of the matrix is induced when the thermal stress induced stress intensity factor exceeds the fracture toughness of the resin. The fracture toughness of the matrix at cryogenic temperature can be improved by controlling the chemical structure, network structure and morphology. Delamination and matrix micro-
cracking are the two common failure modes observed at cryogenic temperature. The amount or density of microcrackings depends mainly on the tensile modulus of fibers and the matrix properties used in the composite. Addition of toughening agents in the matrix decreases the microcracking propensity of these laminates (Timmerman et al. 2002). Glass fibers and epoxy resins are known to be highly loading rate sensitive. The mechanical properties of glass reinforced epoxy composites are found to be rate sensitive even at low strain rates (Sanjee et al. 2005). CFRP structural components used in aircrafts can suffer high and low velocity impact at cryogenic temperature. Fibre reinforcement architecture and stacking sequence play an essential role in the behaviour of composites under such thermal and loading conditions (Rio et al. 2005). At lower speed the there will be more deterioration in the matrix as more time is available for failure to take place results in lower ILSS values which increases with the crosshead speed. At higher loading rates the reduction in ILSS values may be due to the restriction and minimization of relaxation process at the crack tip leading to the growth of stress induced cracks without blunting. The matrix is unable to transfer the load properly due to less availability of time at higher speed
i.e. the load on the matrix is like an impact. Several damage mechanisms may appear such as fibre fracture, matrix cracking, fibre pull-out and delamination. Hence it can be concluded that the laminate requires an optimum time to transfer load effectively through the interface.

These interphases will possess unique properties different from the bulk matrix (Ishida 1990). It can include impurities, unreacted polymer components, non-polymerized additives etc. The thickness and properties of this interphase have crucial impact on the composite properties. The interphase not only allows load transfer between fibers through matrix but also provides a matching of chemical and thermal compatibility between the constituents. A thin rigid inter-phase leads to a low fracture resistance while a thick soft interface results in a better fracture resistance but a lower composite stiffness (Jones 1991). Epoxy resin and E-glass fiber are reported to be loading rate sensitive. The ductility of a matrix resin may become a limiting factor at high strain rate for composite strength. Epoxy resin is more ductile than it’s composite at low strain rate (Padmanabhan 1996). The cryogenic conditioning causes differential contraction
and increases the resistance to debonding by mechanical keying factor (Ray 2005). When cooling from the cure temperature, differences in thermal contraction between the matrix and fiber will generate shear stresses in the resin. When a stress is applied, shear stresses greater than the shear strength of the resin is readily generated and failure of the resin phase will result. When the composite is stressed further by cooling and loading in the cold state, it is likely that there will be resin/fiber debonding. A plastic deformation zone ahead of crack tip region may possible be formed by matrix deformation and micro cracking. A weaker of interfacial bond may result in a low flexural strength of the laminate. The deteriorated integrity can cause low strength at high loading.

Although mechanical strength of most polymers increases or remains same as temperature is decreased, the elongation to failure decreases to extremely low values at cryogenic temperatures. This behavior restricts the use of most polymeric materials at low temperatures. It has been proposed that the local intermolecular rearrangement results in relaxation at low temperature region. The relaxation phenomena are indicating a considerable dependence on
morphology of polymers. There appears to be no definite relationship between the chemical structure of polymers and cryogenic behaviors. Polymers which are able to change their main chain bond angles seem to excel in cryogenic properties. These polymers are flexible and may undergo deformation even when their segmental motions are frozen at cryogenic temperatures. The mechanical properties of E-glass/epoxy composite are rate sensitive at low range of strain rate. It seems that the greater the strain rate and the loading velocity, the greater are the stiffness and ultimate strength of the composite material. Failure strength of glass/epoxy composites increases manifold and failure strain reduces sharply at also high range of strain rate. Loading rate sensitivity seems to be controlled by the area of interfaces and the percentage of polymer matrix phase present in composites. The interphase is defined as a region which is manifested as a result of bonding and reactions between the fiber and the matrix. This region is the site of synergy in composite materials and its influence to overall mechanical properties. Environmental attack can degrade fiber/matrix interface mostly by mechano-chemical principle.
The effect of thermal shock on modulus of Kevlar/polyester sample when it is treated with thermal and cryogenic temperature.

**Fig: 4.30** (A) Effect of thermal shock on modulus of thermally conditioned Kevlar/polyester composites. (B) Effect of thermal shock on modulus of cryogenically conditioned Kevlar/polyester composites.

Toughness value is more due greater amount of shrinkage compressive stress for longer period of time at cryogenic temperature.

The higher ILSS values for cryogenically conditioned samples is attributed to enhanced mechanical keying factor by the generation of cryogenic compressive stresses which enhances the friction at the interface due to contraction of epoxy matrix at low temperature. The composites laminate needs an optimum time to transfer load effec-
tively through the interface. There is an increase in glass transition temperature after cryogenic conditioning of the laminates which may be due incomplete reversibility of molecular chain mobility resulting in reduced chain flexibility.

**Reasonable Remarks**

*Failure is a detour, not a dead-end street.* The structural integrity and durability of fibrous composite acquit the bulletin. Composite, the preamble to the lighter world, have gigantic application from ground based material to the space shuttle. In contrast, a significant mismatch in the environmentally induced degradation of matrix and fiber leads to the evolution of localized stress and strain fields in the FRP composites. The hygroscopic nature of polymeric composite, however, necessitates a complete understanding of the interaction between structural integrity and hygrothermal environments. They absorb moisture in humid environment and undergo dilational expansion. Hygrothermal exposure reduces glass transition temperature (Tg) of polymers and also cause plasticization, resulting reduction in mechanical properties. The presence of moisture and stresses
associated with moisture-induced expansion may cause lowered damage tolerance and structural durability. Mechanical properties of material depend not only on the substrate strength but also on the interface strength. However, moisture absorption and desorption also the reason behind the formation of residual stress. This would modify the local stress threshold required for interfacial debonding, a potential precursor to delamination nucleation. Interfacial debonding (delamination) may cause the premature buckling of the laminate. As the following will demonstrate, composites available in increasingly diverse material forms and manufacturing by an extensive array of moulding and forming processes- have been taken or are poised to take the spotlight in manufacturing arenas throughout the world. In the future the composite technology will play an important role for the development of energy saving vehicles and technologies for environment and climate protection. Carbon fiber reinforced composite is one of the potential material to replace the prestressing steel tendons at low temperature (-27° C) in Canada. Both in the aeronautic and the automotive industry composites are more and more used for crash structures. Advantages of FRP-structure for crash applications are their ability to absorb energy by means of
available numerous absorbing sites. The mechanical properties of composites at low temperatures are influenced by the matrix. At this temperature thermal prestress is crucial. This reduces effective strain to failure and is the source of microcracks in the matrix. The first form of microcracks causes very mild effects in the thermo mechanical behaviour of composites. Considering the influence of low temperature on the fracture micromechanisms in composites; the matrix is brittle and residual tensile stresses in the matrix are promoted. At very low temperature resin embrittlement dominates phenomena and thus composite toughness decreases. As the temperature increases very close to the glass transition temperature of the matrix, it becomes ductile and behaves as softer material.

Composites at low temperature, on the other hand, despite their decades on the venture, are young by comparison and, therefore, not as well known among design and manufacturing engineers. The implication, thus far, is that the composite at low temperature, to mature, must adapt itself to meet the full potential of the inherent empower.

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